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REPORTS ON THE TOTAL SOLAR ECLIPSE OF 1905, AUGUST 30.

(Presented by the Joint Permanent Eclipse Committee of the Royal Society and the Royal Astronomical Society at a Special Meeting of the two Societies, October 19, 1905.)

Report of the Expedition to Castellón de la Plana, Spain.

By H. L. Callendar, M.A., LL.D., F.R.S., Professor of Physics, and A. Fowler, A.R.C.S., Assistant Professor of Physics, Royal College Science, South Kensington. (Received October 19, 1905.)

Part I.—By Professors H. L. Callendar and A. Fowler.

The expedition to Castellón de la Plana, Spain, was one of the series organised by the Joint Permanent Eclipse Committee, the expenses being chiefly defrayed from the Government Grant Fund. Though 23 miles south of the central line, Castellón was selected as the most suitable station after careful inquiries as to the local conditions and facilities had been made by the Vice-Consul, Mr. Edward Harker, who also rendered invaluable aid to the expedition in various other ways. The advantages of being near a town of considerable size sufficiently compensated for the loss of 18 seconds in the duration of totality as compared with that on the central line, and, for some of the work, the resulting change in the position angle of second contact would have been a distinct gain.

The party originally included Mr. W. Shackleton, but in consequence of a temporary illness he was unable to go out to Spain, and the expedition thus suffered the serious loss of an experienced observer at the outset. Mr.

Shackleton had, however, practically completed the large scale coronagraph and prismatic camera which he had intended to use, and it became possible to utilise this apparatus through the voluntary assistance of Mr. E. H. Rayner, of the National Physical Laboratory.

Mr. T. Banfield accompanied the expedition as technical assistant, and Messrs. Isaac Molloy, E. Cahen, and J. J. Steward joined the party as volunteers.

Messrs. Fowler, Banfield, Molloy, and Cahen arrived at Castellón on August 3, and were welcomed at the railway station by a deputation from the Corporation, headed by the Deputy-Mayor, Señor Don Francisco Campos, together with a number of prominent citizens, and Señor Don José Badia, private secretary to the Vice-Consul, who was to act as interpreter. Every possible assistance was promised by the local authorities.

After an inspection of the various sites which had been suggested, it was decided that the greatest facilities were afforded by the grounds of the new Provincial Hospital which is in course of construction. There was ample space enclosed by a high boundary wall, a good supply of cold water, skilled workmen on the premises, and an abundance of completed rooms which could be used as store rooms, photographic rooms, and so on. Permission to establish the camp on this site was readily granted on application to the Deputy-President of the Provincial Deputation, Señor Don Tiburcio Martin.

The work of clearing the ground, building piers for the instruments, and erecting huts was commenced without delay, under the supervision of Señor Don Francisco Tomás, a local architect, who generously performed his own part of the work gratuitously.

During the preparations the Military Governor (His Excellency General Don Juan Manrique de Lara), the Civil Governor (His Excellency Señor Don Sanchez Ortiz), and the Mayor of Castellón made constant inquiries, either personally or by messenger, as to the needs of the expedition; and, in addition, Señor Don José Marza, Town Councillor, was almost constantly in attendance at the camp to ensure that nothing was wanting to facilitate the work.

Professor Callendar arrived at Castellón on August 14 in time to make observations of the full moon; Mr. Rayner on August 17, and Mr. Steward on August 28.

Ten days before the eclipse the necessary drills were commenced and carried on every day at dusk, and also on the two days preceding the eclipse, near the time at which totality would occur.

The weather conditions during the 25 days preceding the eclipse were very promising, there being only three or four days on which good observations would not have been possible. The day of the eclipse, however, was unsettled, and though the first and fourth contacts were observed in perfectly clear sky, not even a glimpse of the sun was obtained during totality. The clouds of early morning were dispersed by a shower of rain, which ceased in ample time for the final adjustment of the instruments, and for records of the prominences before the commencement of the eclipse. These hopeful conditions, however, only persisted for about 30 minutes after first contact, when a great bank of slowly-moving clouds approached from the north-west and completely obscured the sun until totality was at an end. About a minute after totality the crescent sun was seen for an instant, but the obscuration continued with very short breaks until about 20 minutes before the last contact, after which the sky was clear until near sunset.

No results were accordingly obtained during totality, except such as are given by the automatic records of solar radiation and temperature, to which separate reference is made later.

Through the kindness of the Military Governor, a guard of soldiers was stationed in and about the camp on the day of eclipse in order to prevent any possible interference with the work of the observers. It was particularly desired that crowds of people should not be permitted to collect in the vicinity of the camp so that the involuntary shouts to which the phenomena of totality are liable to give rise should not clash with the time signals regulating the exposures of the photographic plates. The arrangements made were entirely satisfactory.

In addition to those otherwise mentioned in this report, the thanks of the expedition are due to Señores Manuel Montesinos (Architect of the Hospital), Telmo Vega (Secretary to the Provincial Deputation), Miguel Peris, and Antonio Gomez, for valuable help in various ways, and to the owners of the numerous factories in the district who stopped work on the day of the eclipse so that there should be no smoke to mar the observations. Special mention should also be made of the invaluable services rendered to the expedition by Señor Badia, who by no means restricted his assistance to that of an interpreter.

Position of Camp and Times of Contact.

The precise geographical position of the eclipse camp was derived from the co-ordinates of a point at the summit of the City Tower as given by the Trigonometrical Survey of Spain,* namely:—

Latitude	39° 59′ 10″·02
Longitude	3° 39′ 0″·33 east of Madrid.

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* 'Red. Geodesica de 1er Orden de España,' Madrid, 1894, p. 45.

The corrections to the camp were very kindly determined by triangulation, by the City Architect, Señor Don Godfredo Ros de Ursinos, with the following results:—

Latitude	39° 59′ 0″·75
Longitude	0° 2′ 47″·52 west of Greenwich.
„	0 h. 0 m. 11·17 s.

Adopting these co-ordinates, and calculating by the approximate formulæ given in 'Nautical Almanac Circular,' No. 19, the following data were found:—

	h.	m.	s.
Eclipse begins August 29	23	55	38 G.M.T.
Totality „ „ 30	1	16	32
Totality ends „ 30	1	19	58
Eclipse „ „ 30	2	35	57
Duration of totality..............		3	26

Angle from north point of 1st contact	295°	Towards east.
„ „ 4th „	114°	

Other calculations gave—

Angle from north point of 2nd contact	137°
„ „ 3rd „	273°
Sun's altitude at mid-totality	54° 40′

The beginning and end of totality, as observed in cloudy sky, were too indeterminate to permit useful records of the times at which they occurred, but Mr. Fowler carefully observed the times of first and fourth contacts by the spectroscopic method, with the following results:—

	h.	m.	s.
1st Contact, G.M.T.	11	55	14
4th „ „	2	35	52

The first contact was thus recorded 24 seconds, and the fourth five seconds, before the respective times calculated. The chronometer error adopted was the mean of two determinations made with a theodolite on the afternoon of the eclipse differing by only two seconds. A more accurate calculation of the times from the Besselian elements given in the 'Nautical Almanac' does not change the results by so much as a second, so that there remains a considerable discrepancy between observation and calculation.

Instruments and Observers.

The general programme of the expedition, which was somewhat extended in consequence of the voluntary assistance of local gentlemen, will be gathered from the following list of instruments and observers:—

20-*Inch Reflector*, with appliances for the measurement of solar and coronal radiation.

H. L. Callendar.

Absolute Recording Bolometer, for normal solar radiation, equatorially mounted.

Horizontal Bolometer, for recording vertical component of total radiation.

Recording Electrical Thermometers, for air temperature, etc.

H. L. Callendar.

Slit Spectrograph, adjusted for the region B to F.

A. Fowler

T. Banfield } Assisting with plate-holders, etc.
Joaquin Garcés }

4½-*Inch Equatorial*, with Evershed solar spectroscope, for visual observations.

A. Fowler.

4-*Inch Coronagraph*, 38 *feet focal length*, with direct-vision prism for coronal and chromospheric spectra.

E. H. Rayner.

I. Molloy, in charge of prism.

Venancio Soto } assisting with plate-holders.
José Babiloni }

3-*Inch Coronagraph*, 57 *inches focal length*, with green screen for inner corona, as suggested by Mr. Shackleton.*

T. Banfield.

3-*Inch Coronagraph*, 20 *inches focal length*, with small polar heliostat, for coronal extensions.

E. Cahen.

Spectrograph of small dispersion, with small cœlostat and image lens for spectrum of outer corona.

Francisco Betoret.

Slitless spectroscopes, for drawings of green ring.

A. Fowler, T. Banfield, Telmo Vega, Francisco Betoret.

2-*Inch Telescope*, for direct observation of corona in the region of a previously selected prominence.

J. J. Steward.

Thermograph and Barograph.

J. J. Steward.

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* 'Monthly Notices, R.A.S.,' vol. 60, p. 433, 1900.

Observations of Stars during Totality.

I. Molloy.

Observations of Shadow Bands.

Juan Vilo.

Time Signals.

J. J. Steward, chronometer.
José Badia. } signals during totality.
Luis Giraudier }

Although the main objects of the expedition were frustrated by clouds, a more extended account of the principal instruments, and of the observations which it was intended to make, may possibly be suggestive on some points in preparing for future eclipses. With regard to the sections not dealt with further, it need only be mentioned that Capella was seen during totality through a break between clouds, and that the fall of temperature indicated by the thermograph was 6°·7 F., while from 30 minutes before to 11 minutes after totality the barograph registered a decided gradual increase of pressure, amounting to 0·02 inch, followed by a slight lowering.

Part II.—By Professor H. L. Callendar, F.R.S.

The 20-inch Reflector.

The mirror made by Common had an aperture of 20 inches and a focal length of 45 inches, giving an image of the sun approximately 1 cm. in diameter. The instrument, as received, had an equatorial mounting with a small slide-holder at the principal focus, and was used by Father Perry for taking photographs of the corona in 1889. In order to adapt it for measuring the heat radiation of the corona, for which purpose the large short-focus mirror was very suitable, the slide-holder was replaced by a diagonal plane mirror, projecting the image to the side of the tube in a convenient position for observation with an eye-piece or a sensitive bolometer or thermopile. The mounting of the telescope was somewhat rough, but after some adjustment of the bearings, it was found to be possible to set the telescope within two or three minutes of the position of any celestial object by means of the circles. As there was no provision for fine adjustment, the eye-piece fitting, carrying the thermopile, was mounted on a sliding plate with a rack-and-pinion movement of sufficient range in right ascension and declination, which proved extremely convenient for the purpose for which the instrument was required. The driving clock at first was very unsatisfactory, but after some alterations to the governor and pinions, it was successfully adjusted to follow for nearly an hour without appreciable error.

The tube of the telescope was fitted with a diaphragm of 15 inches diameter, which limited the aperture, but improved the definition considerably. With this reduction, after allowing for obstruction by the flat, and for loss at the two reflections, the effective concentration of the rays at the focus was upwards of 1000 times, which was ample for the purpose. The mirrors were freshly silvered before packing, about the middle of July, and were necessarily somewhat tarnished by August 30. The loss of heat due to this cause was not serious, and would not have affected the results, as all the measurements were comparative.

The Absolute Recording Bolometer.

This bolometer was designed for the determination of solar radiation in absolute measure by the electric compensation method. The radiation admitted through a measured aperture of 3 sq. cm. was received on a blackened grid of fine platinum strips arranged in such a way as to intercept the whole of the admitted beam. The increase of resistance of the grid, which was nearly proportional to the intensity of the incident radiation, was automatically recorded by means of a Callendar Recorder of the usual pattern. The intensity in absolute measure was determined by observing the value of the electric current required to produce the same rise of temperature in the grid as the radiation to be measured. The bolometer was provided with compensators for eliminating the loss of heat by conduction at the ends of the strips and the effect of changes in the surrounding temperature on the resistance of the grid. The instrument was contained in a cylindrical water-jacket fitted with suitable diaphragms to protect it from air currents, and to limit the radiation received to a small part of the sky in the neighbourhood of the sun. When the instrument was exposed to the sun, a current of water was kept circulating through the jacket to prevent rapid or excessive variations of temperature, and the actual temperature of the water-jacket at any time was recorded by means of an electrical thermometer. The apparatus was mounted on the tube of the 20-inch reflector, and the openings in the roof of the hut were arranged to permit of continuous records being taken between the hours of 10 A.M. and 3 P.M., so as to include the whole duration of the eclipse.

Apart from its use for recording the variations of solar radiation, the instrument was intended for reducing to absolute measure the readings of the coronal thermopile. For this purpose the tube of the telescope was provided with a double cover of tin plate fitted with a series of small apertures which could be uncovered at will so as to admit a known fraction of the full solar radiation to the coronal thermopile. By comparing the readings of the coronal thermopile with the simultaneously recorded readings of the absolute bolometer, it was easy to obtain a factor for reducing the readings of the thermopile at full aperture taken on the moon or the corona to absolute measure.

Incidentally a comparison was made between the readings of the absolute bolometer and one of Angström's pyrheliometers. The two instruments were found to agree very closely in the relative values of the radiation over a wide range, but the readings of the bolometer were nearly 1 per cent. higher than those of the pyrheliometer for a radiation of 1 calorie per square centimetre per minute. This may have been due to some accidental defect of the pyrheliometer, as the values given by the two strips differed by nearly 15 per cent., which appears to be unusual and excessive for this type of instrument.* It might also be explained by an error in the method of reduction, which does not appear to have received attention hitherto. In consequence of the increase of the resistance R of the strip with temperature, the heat C^2R, generated by the compensating current C, increases with rise of temperature, so that it is necessary to use different values of the reduction factor, which are tabulated for different temperatures as indicated by a small thermometer in the instrument. The thermometer, however, merely gives the temperature of the case, and not that of the strip, which must be many degrees hotter when the intensity of the radiation is so great as 1 calorie per square centimetre per minute. In the Angström pyrheliometer it is not easy to obtain the actual temperature of the strip under these conditions, but in the bolometer, the strips of which are of similar width, the rise is found to be upwards of 20° C. By assuming a similar rise of temperature in the pyrheliometer strips above that indicated by the attached thermometer, and employing the appropriate reduction factor, it is noteworthy that the readings of the pyrheliometer would be brought into closer agreement with those of the bolometer.

The Coronal Thermopile.

Previous observations by Langley and Julius had indicated that the heat radiation of the corona must be comparatively feeble, and that it would be necessary to employ the most delicate instruments to measure it with certainty. Langley's observations[*] were made with a straight bolometer strip 1 cm. long and 1 mm. wide, receiving an image of a slit of the same dimensions placed tangentially to a solar image obtained with a siderostat and a mirror of 50 cm. diameter and 100 cm. focal length. But the aperture actually utilised on the corona was limited to 280 sq. cm. by a cat's-eye diaphragm. With this apparatus a negative deflection of 18 scale-divisions was obtained on the body of the moon, and 13 scale-divisions on the corona after eight reflections at silvered surfaces. The difference of 5 scale-divisions appears hardly sufficient to form a satisfactory basis of argument with regard to the nature of the coronal radiation. The objection to the straight slit placed tangentially to the solar image of less than 1 cm. diameter is that a comparatively small portion of the slit receives radiation from the inner corona. A greater effect might evidently be secured by making the bolometer strip in the form of a circular arc embracing the image. Two bolometers of this kind were accordingly made with circular strips, but otherwise of similar dimensions to that employed by Langley. It was found, however, that a current of only one-tenth of an ampère raised the temperature of the strip nearly 20° C., and the variations of zero due to the heating of the strip by the current were too large to permit the employment of a sufficiently sensitive galvanometer to give a deflection of the desired magnitude. Langley is stated to have employed a current of 0·2 ampère in his observations, which would make the heating effect four times as great. The degree of accuracy attainable with a bolometer is limited by the disturbance due to the heating effect of the current. For a given amount of energy expended in heating the strip, the steadiness, other things being equal, will be directly proportional to the surface available for dissipation of heat. Bolometers with a small receiving surface are, for this reason, necessarily less sensitive than large ones. When it becomes necessary to employ a very small receiving surface, as in the case of the corona, it is often preferable to employ the thermoelectric method.

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* Mr. W. E. Wilson, F.R.S., kindly lent me a second Angström pyrheliometer, with which simultaneous comparisons were made. The two strips of Mr. Wilson's instrument differed rather less from each other, but the mean of the two gave a result 7 per cent. lower than the other Angström pyrheliometer.

The thermopile employed by Julius in his observations[†] on the corona in 1901 had a receiving disc 5 mm. in diameter directly exposed to the coronal radiation without the intervention of any mirrors to concentrate the rays or form an image. The thermopile was fixed at the bottom of a long tube with suitable diaphragms, and measured the total effect of the heat radiation from a region of the sky about 3° in diameter surrounding the sun. The differences between the scale readings obtained on the corona and on neighbouring parts of the sky during totality varied from 0 to 8 scale-divisions, but were rendered

[*] 'Astrophysical Journal,' vol. 12, p. 72, 1900.

[†] Published by the Eclipse Committee of the Royal Academy of Amsterdam.

uncertain by the continual passage of light clouds. The sensitiveness of the instrument was such that it would give a deflection of 23 or 24 scale-divisions (estimated) on the full moon, or the equivalent of about 2,000,000 scale-divisions on full sunshine at 1·25 calorie per square centimetre per minute. Assuming that the total radiation of the corona is of the order of one-millionth of full sunshine, one could hardly expect by this method to obtain a satisfactory measurement of its intensity.

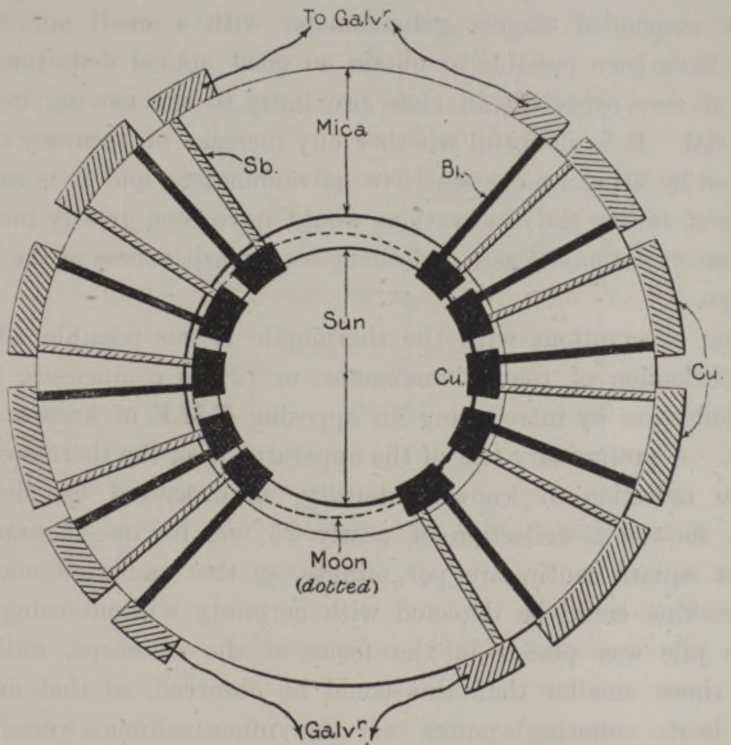
The coronal thermopile, designed for the 20-inch reflector, had a receiving surface consisting of ten small blackened rectangles of very thin copper arranged on the circumference of a circle nearly fitting the image of the sun, so as to receive the greater part of the radiation of the inner corona. The copper rectangles formed the inner junctions of a series of thin bars of antimony and bismuth alloys arranged radially on a thin annular disc of mica. The outer junctions of the couples were formed by thin copper strips at the circumference of the mica disc. The pile was constructed in two halves of five couples each on opposite sides of the disc, and the two halves were connected either in series or opposition through a suitable switch to the galvanometer. The method of construction is shown in fig. 1, but the receiving rectangles were more evenly spaced than as shown in the diagram.

The mica disc carrying the thermopile was suspended in an ebonite ring by means of four thin connecting wires attached to terminals fixed in the ring. The ebonite ring carried on one side a tube sliding in the eye-piece fitting, by which the plane of the thermopile could be adjusted to coincide with the focal plane of the mirror, and on the other side a thick metal tube with diaphragms to screen the thermopile from draughts and from extraneous radiation. The diameter of the innermost diaphragm close to the thermopile was 14 mm., so that only the inner junctions were exposed to radiation. The end of the telescope tube was provided with a double tin-plate cover projecting all round beyond the sides of the tube in such a manner that when the tube was directed on the sun, the eye-piece was perfectly shielded from direct radiation.

Great care had been taken in constructing the thermopile to make all the elements of equal thickness and the copper receiving surfaces of equal area, so that the two halves of the pile might be as nearly equal as possible in sensitiveness and thermoelectric power. In order to test this, the two halves of the pile were simultaneously exposed to the same radiation. The deflection observed when the two halves were opposed was less than one-thousandth part of the deflection obtained when the two halves were connected in the same direction, the radiation remaining unchanged. This accuracy of compensation was very important for the method which it was proposed to adopt. As a subsidiary test, the resistances of the two halves of the pile were measured, and found to be 4·56 and 4·62 ohms respectively. Exact equality of resistance was not essential, but the result is satisfactory as showing how accurately the mechanician, Mr. W. J. Colebrook, of the Royal College of Science, had succeeded in executing the design.

As a result of this accuracy of compensation, the zero of the galvanometer remained extremely steady even under the most trying conditions, with the telescope exposed to full sunshine and surrounded by unequally heated objects. There was never any difficulty in taking accurate observations, provided that the sun was not allowed to shine directly on the eye-piece. At night, and during totality, when the disturbing influence of the solar radiations was absent, it is hardly necessary to say that no trouble was experienced.

Fig. 1.—Coronal Thermopile.



Enlarged about 3 diameters.

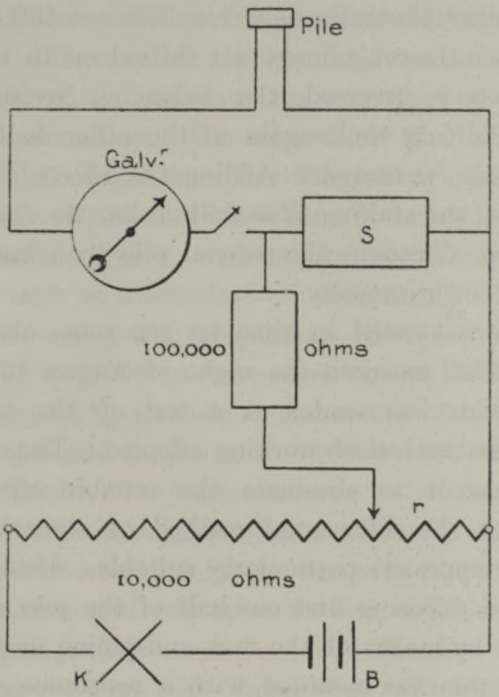
Methods of Observation.

The galvanometer employed with the coronal thermopile was of the movable-coil type with a plane mirror, 1 inch in diameter, reflecting the image of a transparent millimetre scale at a distance of 3 metres into a telescope of 2 inches aperture and 3 feet focal length. With this power the definition was so good that it was easy to read to a tenth of a millimetre with certainty. The galvanometer was supported on a pier south of the telescope and proved extremely steady. The zero seldom shifted by more than a small fraction of a millimetre in the course of the day. The suspension was of very fine phosphor bronze, giving a deflection of 5 cm. nearly for one microvolt with the thermocouple in circuit, so that it was possible to read to 0·002 of a microvolt. A higher degree of sensitiveness, measured merely in scale-divisions per microvolt, might, no doubt, have been obtained by using a suspended magnet galvanometer with a small mirror. But it would not have been possible to obtain so good optical definition or equal steadiness of zero, especially in close proximity to the moving iron tube of the equatorial. It is doubtful whether any increase of accuracy could have been secured by using a more sensitive galvanometer; and it is certain that the trouble of taking the observations would have been greatly increased by the incessant variations of zero and changes of sensitiveness of the suspended magnet type.

In taking observations with the thermopile it was possible either (1) to read the deflection of the galvanometer, or (2) to compensate the galvanometer deflection by introducing an opposing E.M.F. of known value into the circuit. A preliminary test of the apparatus with the thermopile directly exposed to radiation of known intensity, as measured by the absolute bolometer, showed a deflection of nearly 25 cm. for one-thousandth of a calorie per square centimetre per minute, so that radiation one-millionth of full sunshine could be detected with certainty without using a mirror. When the pile was placed in the focus of the telescope, radiation one thousand times smaller than this could be observed, so that even if the intrinsic heat radiating power of the inner corona were only one ten-millionth part of the solar surface, it could still be measured to within 1 per cent.

The direct-deflection method was only suitable for small intensities of radiation. Even for observations on the moon the deflection obtained was far beyond the limits of the scale, and it became necessary to use the compensation method (2). This method, though admitted to be the most accurate, is generally regarded as being too slow and cumbrous for quick work at high pressure, as during totality. It was found, however, that, by a suitable arrangement of apparatus, quicker readings could be secured by the compensation than by the deflection method. The arrangement adopted is shown in the diagram, fig. 2. A battery, B, of known E.M.F., *E*, which was verified at intervals and found to be extremely constant, sends a steady current through a resistance of 10,000 ohms arranged as a potentiometer, so that any convenient fraction r could be tapped off by revolving pointers. The ends of the resistance r were connected through a resistance of 100,000 ohms to a small resistance s in the circuit of the galvanometer and thermopile. The current through the 100,000-ohm circuit would be $Er \times 10^{-9}$, and the P.D. on the small resistance s would be $Ers \times 10^{-9}$, when there was no current through the galvanometer. If r and s were 100 ohms each, and E was 3 volts, the P.D. introduced into the galvanometer circuit would be 30 microvolts, correct to about one part in 1000. The resistances s and r could both be varied from 1 to 1000 ohms, giving a range of ± 1000 microvolts.

Fig. 2.—Diagram of Electrical Connections for Compensation Method.



The obvious advantages of this method, as compared with the usual bridge-wire method, are quickness of manipulation and avoidance of errors due to variation of resistance at the sliding contacts. A more important advantage for thermoelectric work is that the sliding contacts are all in the battery circuit, where there is a relatively large electromotive force, so that accidental thermal effects, due to exposure of the working parts, or sliding friction, or the warmth of the hand, do not affect the galvanometer.

Observations on the Sun and Moon.

Observations were made at frequent intervals on the sun, for the purpose of testing the apparatus, and to serve as data for comparison with simultaneous readings of the absolute bolometer. As an example, when the record of the absolute bolometer showed 1·02 calories per square centimetre per minute for direct sunshine, the same sunshine admitted through a measured aperture 3 mm. in diameter in the cover of the telescope, and adjusted so as to fall on one half of the coronal thermopile, gave an E.M.F. which required the resistances $r = 352$, $s = 100$ ohms to be inserted to balance it. When the sun's image was shifted on to the other half of the pile, and the battery reversed, the balancing resistance required was $r = 348$ ohms. Shifting back again to the other half gave $r = 351$, the resistance s remaining unaltered. Adding the effects observed on the two halves of the pile, and taking $E = 2{\cdot}91$ volts, we find a thermo- E.M.F. of 204 microvolts produced in the coronal pile by a known fraction of the solar radiation of known intensity.

The apparatus was erected in time to get some observations with the coronal pile on the full moon on the night of August 16, shortly before the partial eclipse. This was useful as a test of the sensitiveness of the apparatus and of the method of working adopted. The most essential point in such observations is to eliminate the variable effects of atmospheric radiation, for which the differential method of observation with the two halves of the pile appeared particularly suitable. Using the full aperture of the telescope, and exposing first one half of the pile and then the other to the lunar image by means of the rack-and-pinion motion of the sliding-plate on which the pile was mounted, with a resistance $s = 10$ ohms in the galvanometer circuit, the balancing resistance, r, was found to be nearly constant with a mean value of 290 ohms. The E.M.F. of the battery, E, being 2·92 volts, this was equivalent to a thermo-E.M.F. of 17·0 microvolts for the whole pile, as compared with 204 microvolts obtained on the sun with an aperture of 3 mm., as described in the observation already recorded. This makes the radiation of the full moon, neglecting atmospheric absorption, as in the case of the sun, about 6·6 micro-calories per square centimetre per minute, or about 1/150,000 of that of the sun. The compensation for atmospheric radiation was found to be very perfect, and the sensitiveness ample, as it would have been possible to detect radiation six thousand times smaller than that of the moon. As a further test of the accuracy of compensation for atmospheric radiation, a series of similar readings were taken *in full daylight* at 7 A.M. on the planet Jupiter. These gave a difference of one-fifth of a millimetre deflection in favour of the planet, which could not of course be regarded as a measurement, but illustrates the practically complete elimination of atmospheric effects.

In taking observations on the corona it was intended to apply a similar method, making use of the motion of the moon during totality to define the exact area of the corona corresponding to the differential reading. At the commencement of totality, the thermopile being centred on the sun as indicated in fig. 1, the inner corona on the eastern limb would be fully exposed, while on the western it would be partly covered by the moon, as indicated by the dotted circle. At the end of totality the reverse would be the case. The difference of the readings would correspond to the radiation of the strip of the inner corona uncovered by the motion of the moon between the two readings. The area of the strip of corona considered could be accurately determined from the times at which the readings were taken. The advantage of this method is that it accurately compensates for external disturbances, in addition to giving the radiation from a definite area. It was intended to take as a standard of comparison of similar shape the radiation of the solar crescent a few minutes after and before totality. It would also have been possible to take observations of the total radiation of the corona intercepted by the pile at the middle of totality by connecting the two halves of the pile in the same direction instead of in opposition. But in this case it would have been necessary to take an additional reading with the pile directed to a neighbouring part of the sky to determine the effect of atmospheric radiation, as in the methods adopted by Langley and Julius, and the elimination of atmospheric effect could not for many reasons be regarded as being so perfect.

A number of other readings and comparisons were taken during our stay, on the sun and moon, but the examples already given will suffice as illustrations of the method.

The Horizontal Bolometer.

The horizontal bolometer was of the usual type designed for recording the vertical component of sun and sky radiation. It consisted simply of a pair of platinum thermometers wound on a horizontal mica plate fixed in a sealed glass bulb. One of the thermometers being coated with black enamel is raised to a higher temperature than the other by exposure to radiation. The difference is very nearly proportional to the intensity of the radiation, and is automatically recorded on an electrical recorder of the usual type. It is, of course, necessary for an instrument intended to be exposed in all weathers that the surface receiving radiation should be protected by a glass bulb. It has often been objected that this will cause a very serious error in the record, since glass transmits only a small fraction of the radiation. In practice, however, it appears that this source of error compensates itself. The glass becomes heated and radiates to the enclosed bolometer in practically the same proportion as its absorbs.

This was tested in a very simple manner by making comparisons between the horizontal bolometer enclosed in its glass bulb and the absolute bolometer with the naked strips directly exposed to the same radiation. When the quality of the radiation was varied over a very wide range from a dull-red heat to the highest temperature attainable with an incandescent lamp, it was found that the ratio of the readings of the two instruments remained constant within the limits of error of measurement, showing that the selective absorption of the glass did not materially affect the result. When exposed to the sun and sky the records are not, however, exactly comparable, because the horizontal bolometer takes the vertical component of the total radiation, and measures the whole heat received by a horizontal surface, whereas the absolute bolometer, when equatorially mounted so as to be normal to the sun's rays, records the normal component and receives only a small part of the sky radiation from a region immediately surrounding the sun. The full sky radiation may often amount to 30 or 40 per cent. of the whole vertical component, according to the state of the sky and the altitude of the sun.

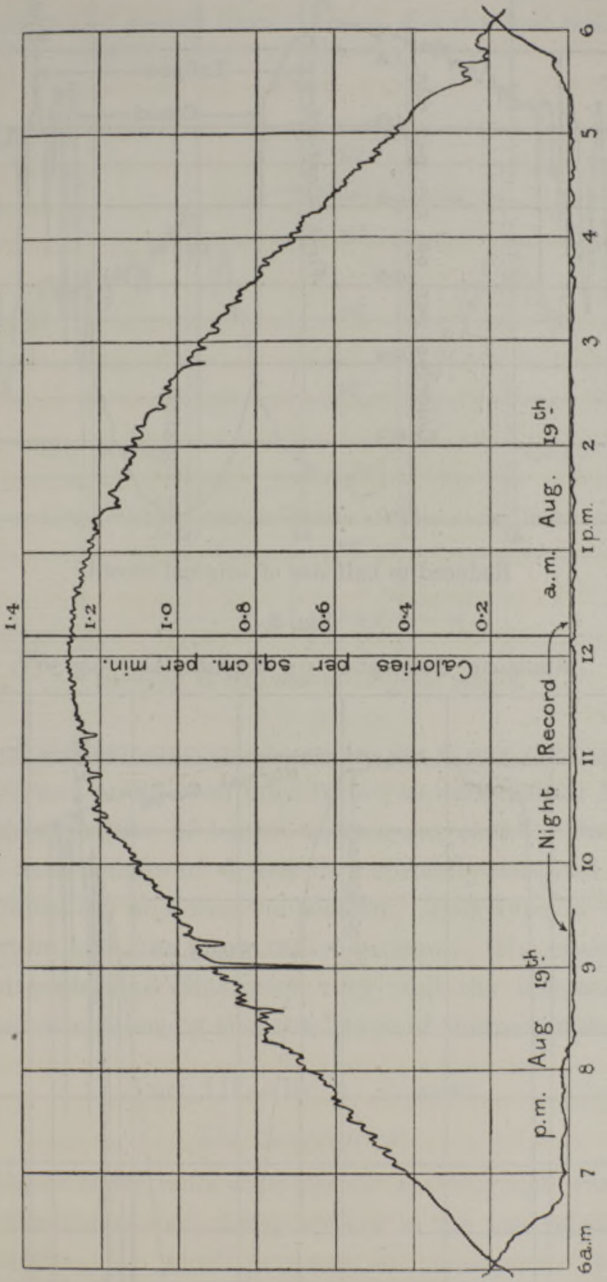
Description of the Records obtained during the Eclipse.

Although the sky was not clear during the eclipse, a description and reproduction of the records obtained may not be without interest, as it is the first time that an attempt has been made to obtain records of radiation and temperature on so large a scale. The record of the Vertical Component obtained with the horizontal bolometer on August 19, reproduced in fig. 3, illustrates the type of curve obtained on a clear day with a sky practically free from clouds. There are always small, incessant variations of radiation, even on the clearest day, which make it necessary to use a recording instrument if comparative results of any accuracy are required.

Fig. 4 shows the record obtained with the same instrument on the day of the eclipse. The heavy shower of rain which occurred about 8.40 A.M. was practically the only rain which fell during our stay. The sky cleared shortly afterwards, and the sun remained clear for half an hour after first contact. When it was obscured, the radiation fell from 1·08 cal. to 0·38 cal., the latter reading showing that the radiation from the cloud was at that time about 35 per cent. of the whole. While the sky remained clouded, the radiation gradually fell to a minimum during totality, and then rose with occasional breaks in the curve, due to variations in the cloud bank. The sun reappeared in time for the observation of the last contact.

Fig. 3.

Vertical Component of Sun and Sky Radiation. Aug. 19th.

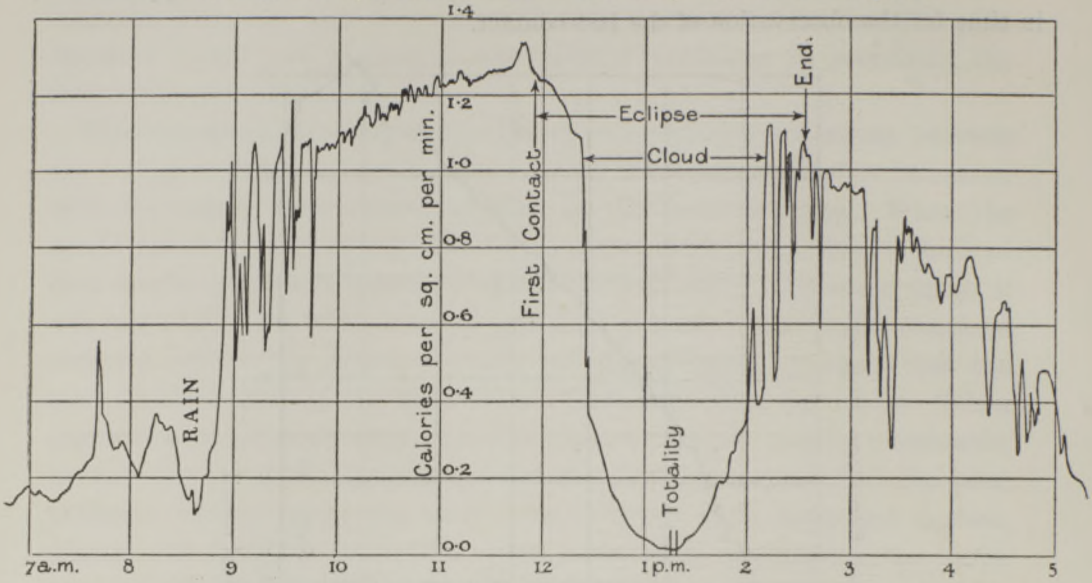


Reduced to half size of original record,

The record with the absolute bolometer shown in fig. 5, extended only from 10.10 A.M. to 2.50 P.M. The normal curve which the record should have followed on a clear day without eclipse is indicated by the dotted line. The record began to fall regularly at first contact, following the predicted

FIG. 4.

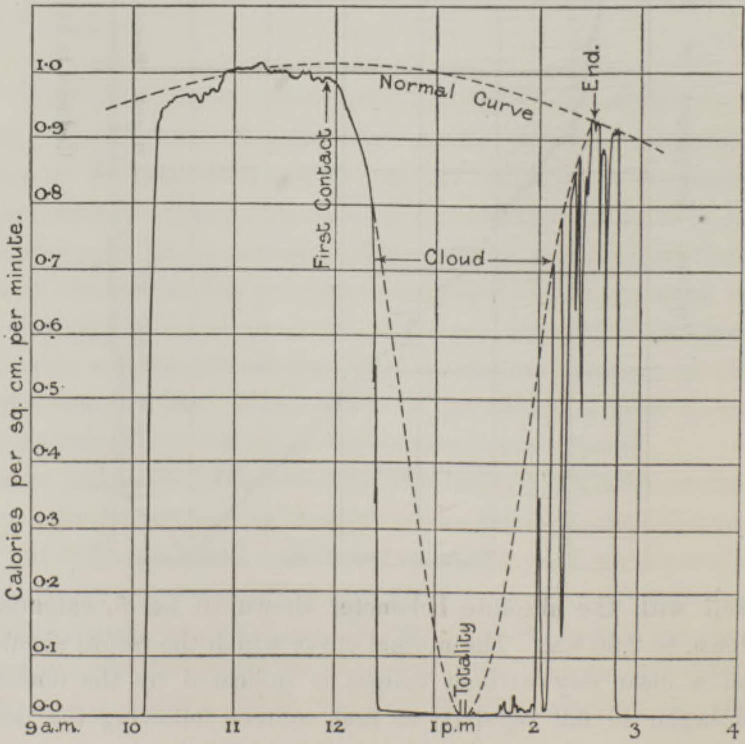
Vertical Component of Sun and Sky Radiation. Aug. 30th.



Reduced to half size of original record.

FIG. 5.

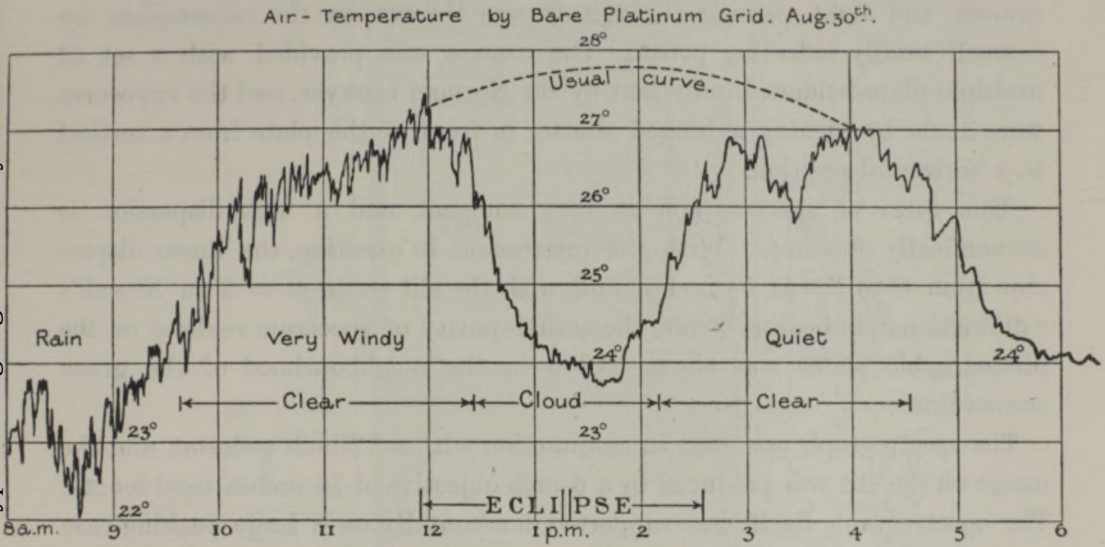
Absolute Bolometer on Equatorial. Aug. 30th.



Reduced to half size of original record.

curve. As soon as the sun was obscured by clouds the reading fell very nearly to zero, because the aperture of the instrument includes only a very small part of the sky surrounding the sun. The dotted curve indicates the course which the record should have taken if the sky had been clear.

FIG. 6.



Reduced to half size of original record.

The record of air-temperature shown in fig. 6 was obtained with a bare platinum wire wound on an open mica frame, as designed for Brown's experiments on the temperature of leaves and air-currents.* The platinum grid was suspended at a height of 4 feet in a specially-designed screen, 1 metre cube, with a double top and free ventilation. This type of thermometer is extremely sensitive and free from radiation error. The scale was 2 cm. to the degree centigrade, and illustrates very well the incessant fluctuations, which are missed altogether by the usual type of thermograph.

Part III.—By A. Fowler.

The Spectrograph.

The special object of the work with the slit spectrograph was to photograph the spectra of the corona and chromosphere in the less refrangible parts of the visible spectrum, for which purpose, in consequence of the possible difficulty of obtaining plates highly sensitive to red light, it was considered advisable to use a prismatic spectrograph of large aperture.

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* 'Roy. Soc. Proc.,' January, 1905, p. 124, vol. B. 76, where a figure is given showing the details of construction. A similar thermometer was made shortly afterwards, with slight differences of detail, to the design of Mr. E. H. Wade, of the Survey Department, Cairo, and has been employed at Helwan Observatory with very satisfactory results.

The instrument employed was of the Littrow type, having an object-glass 3 inches in diameter, one prism of 60° and two of 30°, one of the latter being silvered on the back and adjusted so as to return the light through the prisms and object-glass into the camera. The slit was attached to the side of the camera, and light passing through it was thrown on the object-glass by a small totally-reflecting prism. The camera was provided with a set of multiple plate-holders, kindly lent by Sir Norman Lockyer, and the exposures were made by turning a hinged shutter in front of the plate from a vertical to a horizontal position.

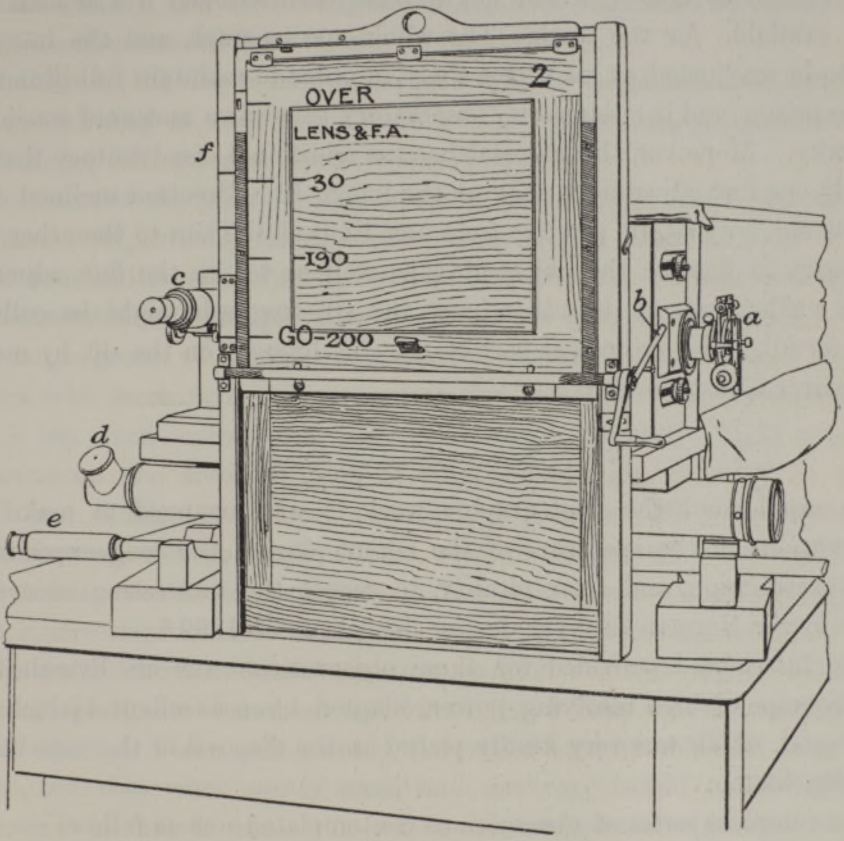
This form of spectrograph is very compact, and a high dispersion is economically obtained. With the instrument in question, the linear dispersion from C to F was $5\frac{1}{2}$ inches, and with the slit set to $m = 2$ on Newall's "diffractional indicator" scale, the actual purity of spectrum realised on the photographic plates was about 13,000 in the neighbourhood of the green corona line.

The spectrograph was used in conjunction with a 12-inch cœlostat, and the image on the slit was produced by a 6-inch objective of 76 inches focal length. The spectrograph itself was supported horizontally on a large packing-case inside a hut, while the object-glass and cœlostat rested on piers outside. The point of second contact in the image formed after reflection from the cœlostat was almost exactly at the extremity of a horizontal diameter, so that the flash spectrum would be depicted under the most favourable conditions, providing that the image could be kept tangential to the sun's limb.

To facilitate the working of the combination, two finders were attached to the spectrograph, one giving a direct view of the sun as seen in the cœlostat mirror, and the other utilising the spectrum reflected from one of the prism faces. The eye-piece of the latter was close to the camera, a mirror being introduced to send the light in the required direction. This arrangement was invaluable, as by its aid one could observe the exact counterpart of the spectrum presented to the photographic plate, and by means of a long rod attached to the fine adjustment of the cœlostat, the position of the sun's image on the slit could be controlled without removing the eye from the finder. No difficulty was accordingly anticipated in photographing the flash spectrum, even with the slit tangential to the sun's limb at the point of contact.

After many trials, made both in England and Spain, the plates selected for use during the eclipse were "Seed" plates sensitised for the visible spectrum by soaking for four minutes in a bath of pinachrome and, after washing in distilled water, drying as quickly as possible. Very promising results were obtained with these plates in experiments on photographing the brighter chromospheric lines before the eclipse.

FIG. 7.—The Slit Spectrograph.



a. Slit.
b. Handle for operating exposing shutter.
c. Finder for viewing spectrum reflected from prism face.
d. Finder for viewing sun in cœlostat mirror.
e. Rod for fine adjustment of cœlostat mirror.
f. Repeating back and dark slide.

The exposures for totality were planned as follows :—

(1)	"Go"	to	200...	For flash spectrum.
(2)	198	,,	190...	For upper chromosphere.
(3)	188	,,	30...	For coronal spectrum, including brighter chromospheric lines for determination of positions.
(4)*	15	,,	"Over"	For flash spectrum.

* Image readjusted between 3 and 4.

It was also intended to make 20 additional exposures on the cusps at intervals before and after totality, but the state of the sky was entirely unfavourable even for this part of the programme.

As a general remark, it may be mentioned that the constantly changing azimuth of the reflected beam of sunlight coming from the cœlostat caused a great deal of labour, which might have been avoided if a siderostat had been available for the work. The whole spectrograph and the image lens had to be readjusted, at least once a day, in order to maintain full illumination of the prisms, and in a temporary observatory this was a matter of considerable difficulty. Moreover, the cœlostat has the additional disadvantage that there is only one fine adjustment, moving the image in a direction inclined to that of the slit, so that, in passing from one limb of the sun to the other, it was necessary to displace the object-glass as well as to use the fine adjustment, With a siderostat, on the other hand, the spectrograph might be collimated once for all, and any desired part of the sun brought on the slit by means of the mirror adjustments.

Spectroscopic Observations.

To supplement the photographic work, it was arranged to make visual observations of the spectrum of the corona during the long exposure with the spectrograph, and, after totality, to repeat the interesting observations made by Sir Norman Lockyer during the eclipse of 1882.*

The instrument provided for these observations was an Evershed solar spectroscope of high resolving power, adapted to an excellent 4½-inch Cooke equatorial, which was very kindly placed at the disposal of the expedition by Mr. Shackleton.

The complete series of observations contemplated was as follows:—

Before Commencement of Eclipse.—To record the appearances and positions of the prominences.

At Beginning and End of Eclipse.—To determine the times of first and fourth contacts by the spectroscopic method.

Shortly Before Totality.—To observe the spectrum of the large spot near the east limb, in order to determine the effect of reduced sunlight, in connection with Evershed's suggestion, that the majority of unaffected lines in the spectrum of a spot may be due to diffused photospheric light.†

During Totality.—(1) To examine the "continuous" spectrum of the corona, especially near *b*, with the view of obtaining further information as to the "ribbed" structure noted by Sir Norman Lockyer in 1882.

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* 'Roy. Soc. Proc.,' vol. 34, p. 296.

† 'Astrophysical Journal,' vol. 5, p. 248.

(2) To observe the structure of a portion of the inner corona as seen with a wide slit in the light of the green line.

(3) To search for the coronal lines between D and the green line suspected by Young and Harkness, and also to search for indications of iron lines.

After Totality.—To note how long the green line could be seen after the end of the totality, and to investigate the relative brightness and extensions of the arc and enhanced lines of iron at the cusps.

In addition to the above, half a minute was to be devoted to sketching the green coronal ring as seen with a direct-vision spectroscope of considerable dispersion, the collimator of course being removed.

On account of the unfavourable weather, only a very small part of this programme was actually carried out: namely, the determination of the times of first and fourth contacts, details of which have already been given, and the observation of the prominences before the eclipse commenced.

The large group of prominences on the eastern limb, reported by all observers who were favoured with clear sky, was well seen between 10.35 and 11.5, but even more interesting was a small intensely bright metallic prominence on the western limb, at a position angle recorded as 306°, counted from north through east. In the spectrum of this prominence, the *b* and D lines were exceptionally bright, as were also a great number of other lines ordinarily seen in such eruptions. The observations may possibly be of interest in investigations of the coronal structure in this region, and in case of error in the determination of absolute position angle, it may be useful to add that the eruption was about 149° from the middle of the large group, reckoned through the north point. Several other prominences were also observed, but they were mostly small and not very bright. As a general remark, it was noted that the whole chromosphere appeared to be considerably disturbed, and reversals of the D lines were observed in unusually high solar latitudes.

It may be added that considerable activity was shown in the large spot near the east limb. The C line was reversed and distorted in several places, and D_3 was distinctly visible as a dark line in the neighbourhood of the spot. On the day after the eclipse similar appearances were again seen at C and D_3, and the D and *b* lines were clearly reversed over the umbra.

Part IV.—1. By W. Shackleton, A.R.C.S., F.R.A.S.

40-*foot Coronagraph and Prismatic Camera.*

Originally it was intended that the coronagraph used by Mr. Maunder in Mauritius[*] should form part of the equipment of the expedition, but towards the middle of May Mr. Maunder received an invitation to join the Canadian expedition to Labrador, and it was agreed that he should again have the use of this coronagraph.

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[*] 'Roy. Soc. Proc.,' vol. 69, p. 256.

The replacement of an instrument for this work at so late a date was a serious embarrassment, but fortunately the expedition was helped out of the difficulty by the generosity of Dr. Copeland, who kindly placed at our disposal the 40-foot lens and large direct-vision prism which he had successfully used in 1898 and 1900.

It was decided to use the instruments according to Dr. Copeland's plan, viz., to use the lens alone as a coronagraph during the greater part of totality, and conjointly with the prism as a prismatic camera near the beginning and end of totality.

Instead of pointing the instrument to the sun or using a stationary mirror, however, it was proposed to employ a cœlostat and keep the camera horizontal, using stationary plates.

The equipment therefore consisted of—

(i) A Dallmeyer lens 38 feet 6 inches focal length of 4-inch aperture.

(ii) A D.V. prism, direct for λ 3890, of about 4-inch clear aperture. This was mounted on a platform in front of the objective, and could be inserted or withdrawn as required.

(iii) A 12-inch cœlostat.

(iv) A camera for use with above, as described below.

In order to provide for the daily change in azimuth of the reflected solar beam from the cœlostat, it was arranged that the objective and plate-holder should be connected together by a rigid camera body, in order that the two might be moved sympathetically.

This body was built up of tapered lattice girders (of mild steel) for sides, with similar lattice bracings top and bottom; the whole unbolted into four flat pieces for transport.

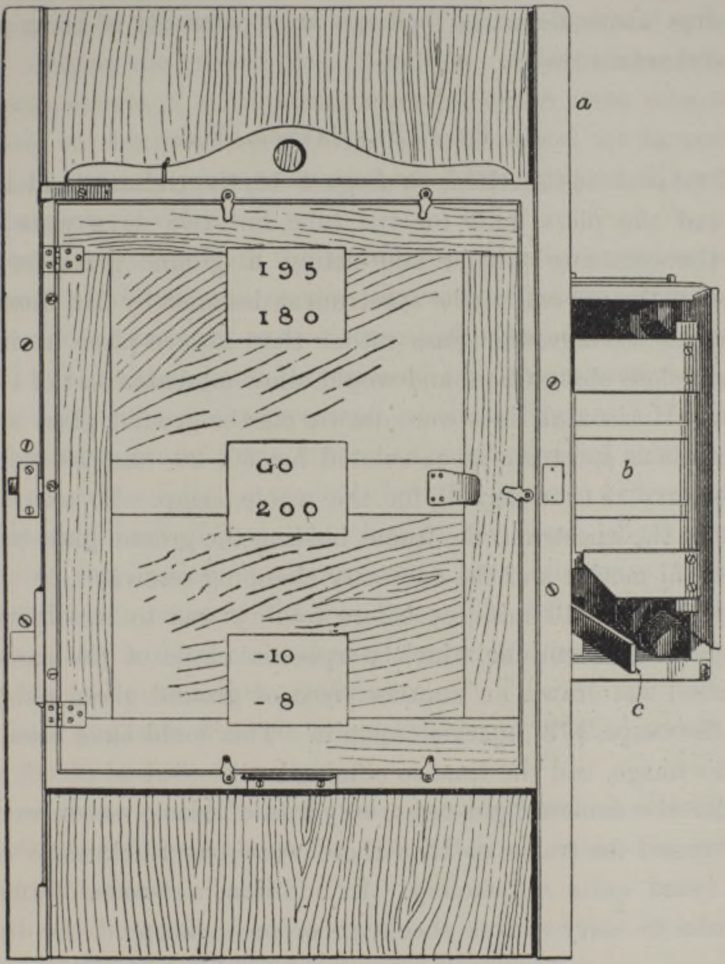
Each end of this skeleton tube was lined with a mahogany box for a distance of about 4 feet. The one at the narrow end carried the object-glass, immediately in front of which was the platform for supporting the prism. At the wider end an adjustable sliding box, divided into a large and small chamber by an inner partition, fit into the outer mahogany lining; a repeating back, into which the plate-holder fitted, was attached to the larger of these chambers, whilst the smaller chamber was provided with ground glass at the camera end, the other end being open to the object-glass; the use of this latter portion is explained below.

For making the exposures a balanced double-flap shutter was designed;

this was contained in the larger chamber, a few feet in front of the plate, and was operated by a lever.

As explained previously, it was intended that the prism should be drawn in front of the object-glass at the beginning and towards the end of totality,

FIG. 8.—Camera end of 40-foot Coronagraph and Prismatic Camera.



a. Repeating back and dark slide.
b. Ground glass screen for observation of less refrangible part of spectrum.
c. Handle for operating exposing shutter.

when photographs of the coronal and flash spectra were to be taken on plates 6 × 15 inches, the longer edge being in the direction of dispersion. This length of photographic plate was only sufficient to include the spectrum from about H_β to some part in the ultra-violet, and the visible portion of the spectrum fell on the ground glass attached to the small chamber on the right of the plate-holder; hence the spectroscopic phases of the eclipse could be visually observed and simultaneously photographed; by this means it was anticipated that the flash spectrum might be secured both at the beginning and end of totality. During the greater part of totality the prism was to be removed, and photographs of the corona obtained on plates 12 × 15 inches.

It is only to be regretted that the weather proved unfavourable, and that the apparatus above described had not an opportunity of being put into use and its novel points tested.

2. By E. H. Rayner, M.A.

When I arrived at Castellón, on August 16, the cœlostat had already been adjusted and the piers built for the tube, but two days were occupied in adapting the exposing shutter and fitting a ground glass for the visual observation of the red end of the spectrum as designed by Mr. Shackleton. It was decided to use a ground glass rather than an eye-piece, as it would not require such close observation, and would allow a greater part of the spectrum to be seen. Horizontal lines were drawn on the ground glass at the limits of the continuous spectrum as calculated for 60, 20, and 10 seconds before totality, to serve as time signals for the whole camp. To accurately adjust these lines to the spectrum, the frame holding the ground glass was provided with a vertical motion and the necessary clamping screws.

Another signal at 10 minutes before totality was to be observed on the direct image of the sun, for which purpose a circle of the same diameter, 4 3/16 inches, was drawn on another piece of ground glass, and the angular extent of the cusps, 178°, marked upon it. This could have been superposed on the sun's image, and the time so obtained.

To render the camera light-tight, 60 yards of black sateen were wrapped in a spiral round the frame, so that there were two thicknesses everywhere. This was found quite satisfactory. In addition, a wooden frame was built over the tube to carry canvas sheets, in order to keep off the direct rays of the sun.

Considerable difficulty was experienced with the cœlostat clock, the sun's image in the camera having at first an oscillating motion of $\frac{1}{4}$ inch every two minutes, corresponding with the period of the driving screw. As the result of some days' work, however, this was reduced to about 1/30 inch. To produce this improvement, the socket in the worm wheel on the driving screw spindle was filed on one side and packed with a small piece of metal on the other, and both worm and driving screw had to be pressed so tightly into the parts driven by them that the clockweight had to be doubled. The further diminution of the periodic error which appeared, without anything being done except the running of the clock in the usual course of trials, may probably be attributed to the action of dust in grinding the parts to a better fit.

"Squaring-on" the objective was very easily and quickly done by observation at the camera end of the images of a small electric torch reflected from the various surfaces of the lens.

Visual focussing of the sun on the ground glass was found to be greatly facilitated by keeping the ground glass in motion. By this means fine detail, such as the components of a dispersing sun spot, which were otherwise completely invisible on the ground glass, became very useful for focussing upon. This was in fact the only practicable method of focussing on the sun's image with the apparatus provided.

Attempts were made to obtain the actinic focus by direct exposure of very slow plates on the sun, but the results were unsatisfactory in consequence of over-exposure and air tremors, and recourse had to be made to photographing a star. The brightest that could be projected into the camera was γ Aquilæ, and the results showed a close agreement between actinic and visual focus.

A thorough investigation of any difference between visual and actinic focus of such a lens might usefully be made before the departure of an expedition, as a temperature change of some 3 inches in the focal length necessitates visual focussing just before exposure, with any allowance that may be required for difference between the two foci. The definition of the lens and mirror combined left nothing to be desired, and would well repay the greatest care taken with the mechanical adjustments.

It is also very desirable that the interesting point of change of focus with temperature should be fully investigated.

It may be useful to put on record the exposures which were decided upon. They are given in "eclipse times" in the following table, the duration of totality being 205 seconds.

Number of plate.	Begin.	End.	Remarks.
1	−10	− 8	For spectrum.
2	"Go"	200	„
3	195	180	„
4	170	150	Prism removed for corona.
5	140	85	„ „
6	75	65	„ „
7	55	25	Prism inserted for spectrum.
8	22	15	„ „ „
9	10	"Over"	„ „ „

Sir William Abney's intensity scales were impressed on the corona plates by the light of a standard candle on the night before the eclipse.

Mention should be made of the fact that had the clouds cleared away sufficiently soon to allow of photographs being taken during totality, valuable time would have been required to set the image properly in the camera, as the clock had no maintaining power to keep the image in position during the necessary windings.

The general design of the apparatus was very satisfactory, but a half-plate focal plane shutter, adapted for trial photographs of the sun for focussing purposes, would be a valuable addition.

Total Eclipse of the Sun, 1905, *August* 30. *Preliminary Account of the Observations made at Sfax, Tunisia.*

By Sir William Christie, K.C.B., Astronomer Royal.

(Received October 16, 1905.)

I. *General Arrangements.*

An expedition to observe the total solar eclipse of August 30 having been sanctioned by the Admiralty, it was arranged, in concert with the Joint Permanent Eclipse Committee, that a party from the Royal Observatory should make observations at Sfax, a town on the north coast of Africa, about 150 miles south of Tunis. The programme of observations consisted of photographs of the corona on various scales for coronal detail and streamers, and photographs of the spectrum of the corona and chromosphere.

The observers from Greenwich who took part in the expedition were Sir William Christie, Mr. Dyson, and Mr. Davidson. Professor Sampson, Mr. J. J. Atkinson, and Captain Brett, D.S.O., generously volunteered their assistance and shared the work of erecting and adjusting the instruments as well as of the observations on the day of the eclipse.

The Admiralty gave instructions that H.M.S. "Suffolk" should convey the observers and instruments from Malta to Sfax and should assist in the preparations and in the observations on the day of the eclipse. The expedition is greatly indebted to Captain Beatty, D.S.O., and to the officers and men of the "Suffolk" for their assistance and hearty co-operation.

We are indebted to M. Fidelle, Controleur and Vice-Consul (the representative of the French Government) and to the Mayor and Municipality for a

The Fluted Spectrum of Titanium Oxide.

By A. Fowler, A.R.C.S., F.R.A.S., Assistant Professor of Physics, Royal College of Science, South Kensington.

(Communicated by H. L. Callendar, M.A., LL.D., F.R.S., Professor of Physics, Royal College of Science, S.W. Received May 18,—Read June 20, 1907.)

[Plate 6.]

In a previous paper* it was shown that most of the dark flutings which are characteristic of the spectra of Antarian or third type stars correspond with flutings which appear in spectra obtained from oxide and chloride of titanium, but it was then uncertain whether the flutings originated in the vapour of the oxide or in that of the metal itself.

The purpose of the present communication is to give an account of the observations which have led to the conclusion that the flutings in question are produced by a compound of titanium with oxygen, and to give a revision of the table of wave-lengths based upon photographs taken with increased dispersion.

The Oxide Origin of the Flutings.

The general principle underlying the investigation was the very simple one that if the "Antarian" flutings were due to the *element* titanium they should appear, under favourable conditions, in the spectra of compounds of the metal with different elements, whereas if they were produced by the *oxide* they would only appear when the metal was combined with oxygen, or was able to combine with it during the experiment.

The most decisive results have been obtained from experiments with titanium chloride ($TiCl_4$), a heavy volatile liquid, the vapour of which rapidly combines with oxygen on exposure to moist air and forms dense fumes of titanium oxychloride. On account of this affinity for oxygen, considerable care is necessary in attempting to obtain the spectrum of the chloride without contamination with that of the oxide. The observations have shown, however, that not only is the spectrum of the chloride free from the Antarian flutings, but that it is characterised by a perfectly different group of flutings in the blue which does not occur in the stellar spectra. This "chloride group," as it may be conveniently called for purposes of reference, is a somewhat complicated cluster of flutings fading towards the violet, having three principal heads at wave-lengths 4199·5, 4192·7, and 4188·0, of which the middle one is the brightest.

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* 'Roy. Soc. Proc.,' vol. 73, p. 219, 1904.

Experiments with metallic titanium have also indicated that the Antarian flutings are only produced in the presence of oxygen. Particulars of the experiments are as follows:—

(1) Vacuum tubes containing the vapour of titanium chloride were prepared in the usual manner, but it may be remarked that, in consequence of the low conductivity of the vapour, the most satisfactory results were obtained with tubes giving a total length of discharge not exceeding two inches. When the capillary tube was very narrow, little more than a line spectrum was observed, even when there was no jar in the circuit; there was just a trace of the chloride flutings already mentioned, and enhanced as well as arc lines of titanium were well brought out. In the spectrum of the bulb, however, the chloride group was a conspicuous feature, and enhanced lines were not seen, while arc lines were numerous. When a tube of wider bore was chosen, the spectrum of the capillary corresponded very closely with that of the bulb in the previous experiment. In each case, the passage of the jar spark resulted in the appearance of the line spectrum of chlorine and the almost total suppression of that of titanium.

No traces whatever of the Antarian flutings were obtained in these experiments, although the presence of the chloride group of flutings indicated that the electrical conditions in some cases were not unfavourable for their production, if their existence depended only upon the presence of titanium.

(2) The spectrum of titanium chloride was further investigated by introducing some of the liquid into a tube containing dry nitrogen at atmospheric pressure.

A tube 2 cm. in diameter and about 10 cm. in length was sealed at one end and provided with platinum electrodes, having a sparking distance of about 1 cm. Through a rubber stopper at the other end two smaller tubes were passed, one for the admission of any desired gas and the other for the escape of the gas driven out. The admission tube was of ⊢ form, and attached to the vertical arm by a rubber connection was a previously prepared tube containing a small quantity of titanium chloride. This receptacle consisted of a piece of glass tubing about 3 cm. long, drawn out and sealed at its lower end, and scratched with a file so that it might be easily broken; a short piece of rubber tubing was attached at the other end, and when a sufficient quantity of the liquid had been poured in to fill both glass and rubber tube, the latter was closed with a pinch-cock. In this way a sample of the liquid practically free from oxide was secured, and it could be introduced into the sparking tube when desired without further exposure to the external air.

The apparatus having been thoroughly dried by a current of warm dry air, it was filled with nitrogen, and the titanium chloride was then admitted by breaking off the end of the tube containing it. Even after all the precautions taken to exclude moisture, there was a very slight formation of fumes on the exposure of the liquid, which, however, subsided in a few minutes. On passing the spark (without jar) numerous lines of titanium and the chloride group of flutings were seen, but there was no trace of the Antarian series of flutings. When the jar spark was passed, the chloride flutings were abolished, and enhanced lines of titanium were strongly marked.

To carry the experiment a stage further, the nitrogen was replaced by dry oxygen, and the trace of oxychloride fumes again resulting from residual moisture was allowed to subside. On passing the spark the Antarian series of flutings formed the most prominent feature of the spectrum, but the chloride group was also visible.

(3) A similar experiment in which the sparking tube was filled with dry hydrogen gave an identical result. That is, the chloride group of flutings was visible, while the Antarian series was absent. In this experiment a purple deposit, presumably of titanous chloride (Ti_2Cl_6), was formed on the walls of the tube.

(4) Experiments on the *arc* spectrum of titanium chloride (on iron poles) in an atmosphere of dried nitrogen were also made. Under these conditions, the line spectrum of titanium and the chloride group of flutings were well developed, but the Antarian flutings were excessively feeble and the traces observed were probably due to residual oxygen or moisture, as a thin white deposit was formed on the poles. With an atmosphere of oxygen, however, the Antarian flutings came out strongly.

(5) In another series of experiments, the arc was passed between iron poles, charged with metallic titanium, in an atmosphere of dried nitrogen. Only feeble traces of the Antarian flutings were seen, and these may again be sufficiently accounted for by residual oxygen or moisture. The flutings, however, were well developed when oxygen or air were substituted for nitrogen, but in neither case was the chloride group observed.

(6) As already noted in the previous paper, the Antarian flutings are also visible under the following conditions:—

(*a*) Arc in air between carbon poles well charged with oxide of titanium, the flutings being best seen in the "flame" when the arc is long.

(*b*) Spark, without jar, through fumes of oxychloride of titanium; with a spark of suitable intensity, the line spectrum is almost eliminated, but there is a continuous spectrum of considerable strength which doubtless arises from particles which are incompletely volatilised.

(*c*) Oxy-coal-gas flame, fed with the fumes of titanium oxychloride; the flutings are in this case not easily seen on account of the bright continuous spectrum which is also present.

These observations do not seem to admit of any other conclusion than that the flutings represented in the spectra of Antarian stars are produced by a compound of titanium with oxygen, and not by the vapour of the metal itself.

The result is of some importance as indicating that the source of the fluted absorption in the Antarian stars is at a temperature low enough to permit the formation of a chemical compound, and also as demonstrating the presence of oxygen, of the existence of which in these stars there is otherwise no direct evidence. The investigation has lately gained additional interest in consequence of Professor Hale's discovery of some of the less refrangible flutings in the spectra of sun-spots.*

The Wave-lengths of the Flutings.

The identification of the flutings of the Antarian stars with those of titanium rested upon such a great number of apparent coincidences in position, and similarity of appearance, that it was almost independent of a very precise knowledge of the wave-lengths, and was sufficiently justified by the wave-lengths derived from photographs taken with the moderate dispersion then available. No further determinations of the positions of the stellar bands have been published, but the application of a more powerful spectrograph has made it possible to determine the wave-lengths of the terrestrial flutings with much greater precision. The instrument employed was a very efficient one of the Littrow form, having one prism of 60° ($\mu_D = 1{\cdot}6467$) and a focal length of 12 feet, the effective aperture employed being 1½ inches. The spectrum is photographed in sections on plates 12 × 2½ inches, and the linear dispersion ranges from 16 tenth-metres per millimetre at λ 7100 to 2·7 tenth-metres per millimetre at λ 4350. With this dispersion the heads of many of the flutings are found to be more complex than was formerly suspected, but neither this nor the corrections of the wave-lengths affects the probability of identity with the stellar flutings.

Many experiments have been made in order to produce the fluted spectrum as free as possible from superposed lines. The uncondensed spark passed through the fumes from titanium chloride is possibly the best way of obtaining this result, but the photographic registration with high dispersion is difficult. The most convenient method yet found is to volatilise titanium oxide in the electric arc between iron poles, and the photographs reproduced in Plate 6 were obtained in this manner.

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* 'Astrophysical Journal,' vol. 25, p. 75, 1907.

Under these conditions, the "line" spectrum of titanium is not strongly marked, and iron is only represented by the brighter lines of its flame spectrum. Nearly all of these metallic lines appear on the more refrangible side of D, and are strongest towards the blue. The flutings which occur in the flame of the iron arc do not appear to contribute appreciably to the combined spectrum of iron and titanium oxide. Incidentally, the photographs admirably illustrate the simplicity of the line spectrum of iron in the arc-flame.

For the determination of wave-lengths, the reference lines employed were those of iron and titanium occurring with the flutings, whenever suitable lines were available for the purpose. In many cases, however, and in the whole region on the red side of D, the reference lines were selected from a spectrum of the iron arc photographed in juxtaposition with the fluted spectrum; the shutter for exposing the two parts of the slit was entirely detached from the spectrograph, and there was no evidence of relative shift of the two spectra in the plates measured.

The adopted positions of the reference lines were those given by Rowland in his table of solar spectrum wave-lengths, and the interpolation was made in the usual manner by the Cornu-Hartmann formula. For the part of the spectrum less refrangible than 6860, in which Rowland does not tabulate any lines of iron, lines of the arc spectrum were first identified with solar lines and the corresponding solar wave-lengths adopted. The wave-lengths given in the table are stated to two places of decimals, except in the extreme red, where the dispersion is relatively small, and in cases where the edges of the flutings are not very sharply defined.

No attempt has yet been made to tabulate the thousands of fine "structure lines" which compose the flutings, but all the "heads" and "sub-heads" which could be identified as such have been included. Some of the more marked details in the heads, probably consisting of relatively strong structure lines, or clusters of such lines, have also been measured; for want of a better term, they are described as "maxima." The classification into heads and sub-heads is somewhat arbitrary in many cases, and it should be explained that some of the heads are classed as such, not because they are prominent features of the spectrum, but because of their probable association in series with stronger heads in the groups to which they belong.

With the high dispersion employed, the heads of some of the fainter flutings, especially in the region more refrangible than F, almost lose their distinctive characteristics, and their identification has only been possible in some cases by comparison with photographs taken on a smaller scale. It has been considered desirable to include these for reference in comparisons with stellar spectra, which are usually photographed with moderate dispersion, and also because of their possible use in investigations of the series relationships of the various flutings.

The relative intensities of the flutings are roughly shown by the numbers in the second column of the table, and an attempt is made in the third column to indicate the general characteristics by symbols having the following significance:—

(*a*) The fluting fades out rapidly, and is not clearly resolved with the dispersion employed. These appear as lines with a slight shading towards the red.

(*b*) The fluting fades away more gradually, and the structure lines are very closely crowded together.

(*c*) The fluting resembles those of class (*b*), except that the structure lines are more clearly separated.

(*d*) The structure lines are widely separated, and extend over a long range.

For convenience of description in the table, the flutings are classed in numbered groups, into which the spectrum seems naturally to divide itself. It is not possible, however, to convey an adequate idea of so complex a spectrum by means of a table alone, and reference should be made to the reproductions of the photographs given in Plate 6. The first four strips, representing the spectrum from 4580 to 7200, have been enlarged 1·8 times from the original negatives, and the attached scale of wave-lengths will facilitate comparison with the table. Lines due to iron are separately indicated, as also are those arising from impurities of sodium, calcium, and lithium in the material employed. The superposition of iron lines on the flutings beginning at 4954·8, 5167·0, and 5448·5, tends to conceal the character of the heads, and reproductions of photographs taken with carbon poles are accordingly given in the fifth strip, the enlargement here being 3·5 times. In this case most of the iron lines are absent, but titanium lines are generally more numerous throughout the spectrum.

The photographs of the less refrangible parts of the spectrum were taken on Messrs. Wratten's "Verichrome" and "Panchromatic" plates, which gave uniformly good results.

The Fluted Spectrum of Titanium Oxide.

Wave-length.	Intensity.	Character.	Remarks.
4353 ·68	2	*d*	1st head of 14th group.
4395 ·05	2	*d*	2nd head.
4421 ·66	1	*d*	Sub-head.
4436 ·68	2	*d*	3rd head.
4462 ·34	3	*d*	1st head of 13th group.
4462 ·70	3	—	A "maximum" in head.
4506 ·08	2	*d*	2nd head.
4506 ·62	2	—	A maximum in head.
4548 ·04	2	*d*	3rd head.
4548 ·30	2	—	A maximum in head.
4584 ·62	3	*d*	1st head of 12th group.
4584 ·92	3	—	A maximum in head.
4586 ·78	3	*d*	Sub-head.
4587 ·20	3	—	A maximum in sub-head.
4626 ·49	4	*d*	2nd head.
4628 ·68	4	*d*	Sub-head.
4668 ·82	4	*d*	3rd head.
4669 ·19	4	—	A maximum in head.
4671 ·26	3	*d*	Sub-head.
4671 ·66	3	—	A maximum in sub-head.
4761 ·08	5	*d*	1st head of 11th group.
4761 ·37	5	—	A maximum in head.
4761 ·86	5	—	„ „
4764 ·52	5	*d*	Sub-head.
4804 ·55 }	5	*d*	2nd head, included in cluster.
4805 ·61 }			
4807 ·42	4	*d*	Sub-head.
4848 ·20 }	3	*d*	3rd head, included in cluster.
4849 ·03 }			
4893 ·00	2	*d*	4th head.
4954 ·78	6	*d*	1st head of 10th group, sharply defined.
4955 ·26	6	—	A maximum in head.
4957 ·21	6	*d*	Sub-head.
5002 ·88	3	*d*	2nd head } Identification difficult with high dispersion.
5050 ·5	3	*d*	3rd head ?
5167 ·00	7	*d*	1st head of 9th group, sharply defined.
5167 ·50	7	—	A maximum in head (not Mg line).
5169 ·51	7	*d*	Sub-head.
5240 ·71	5	*d*	2nd head, structure lines very wide apart.
5241 ·00	5	—	A maximum in head.
5307 ·92	3	*d*	Sub-head.
5308 ·14	3	—	A maximum.
5356 ·21	2	*d*	Sub-head.
5356 ·86	2	—	A maximum.
5359 ·07	3	—	A maximum, or ? sub-head.
5359 ·51	2	—	A maximum.
5361 ·22	3	—	„
5391 ·05	2	—	A maximum, or ? sub-head.
5448 ·48	7	*d*	1st head of 8th group, sharply defined.
5449 ·07	7	—	A maximum in head.
5451 ·32	7	*d*	Sub-head.
5496 ·79	5	*d*	2nd head.

Wave-length.	Intensity.	Character.	Remarks.
5597 ·92	10	*a*	1st head of 7th group, sharply defined.
5603 ·98	5	*b*	Sub-head.
5629 ·53	8	*a*	2nd head.
5635 ·54	5	*b*	Sub-head.
5661 ·68	6	*a*	3rd head.
5667 ·81	4	*b*	Sub-head.
5694 ·56	5	*a ?*	4th head.
5728 ·13	4	*a ?*	5th head.
5760 ·15	4	*b*	1st head of 6th group (followed by Ti 62 ·48 and Fe 63 ·22).
5790 ·86	4	*b*	Sub-head.
5811 ·28	4	*b*	2nd head.
5815 ·14	4	—	A maximum, or line.
5846 ·70	4	*b*	Sub-head.
5863 ·55	4	*b*	3rd head (probably).
5872 ·9	3	*b*	Sub-head.
5905 ·1	3	*b*	„
5954 ·66	3	*b*	1st head of 5th group (relatively inconspicuous).
6006 ·5	3	*b*	2nd head.
6057 ·6	2	*b*	3rd head.
6149 ·2	5	*a ?*	A doubtful head.
6158 ·86	10	*a*	1st head of 4th group.
6162 ·37	8	—	Sub-head ? Perhaps wholly Ca line.
6174 ·60	10	*a*	2nd head.
6183 ·83	4	*b*	Sub-head.
6186 ·77	8	*a*	3rd head.
6190 ·07	5	*b*	Sub-head.
6215 ·35	8	*a*	4th head.
6222 ·72	6	*b*	5th head.
6268 ·35	4	*b*	Sub-head.
6275 ·70	3	*b*	„
6321 ·0	2	*c*	„
6321 ·8	2	—	A maximum in sub-head.
6350 ·6	2	*b*	Sub-head.
6357 ·9	3	*c*	1st head of 3rd group (relatively inconspicuous).
6384 ·4	3	*c*	2nd head.
6400 ·1	2	*b*	Sub-head.
6416 ·0	3	*b*	3rd head.
6448 ·2	4	*b*	4th head.
6479 ·4	4	*b*	5th head.
6484 ·0	4	—	Sub-head ? or cluster of lines.
6512 ·8	4	*b*	6th head.
6544 ·5	4	*c*	7th head.
6550 ·2	4	—	A maximum.
6551 ·8	4	—	„
6562 ·5	3	*c*	Sub-head.
6579 ·5	3	*c*	„
6594 ·5	3	—	A maximum.
6626 ·3	3	—	„
6634 ·4	3	*b*	Sub-head.

Wave-length.	Intensity.	Character.	Remarks.
6651 ·5	8	*b*	1st head of 2nd group.
6681 ·0	8	*b*	2nd head.
6714 ·1	8	*b*	3rd head.
6748 ·0	8	*b*	4th head.
6782 ·0	8	*c*	5th head.
6815 ·1	5	*c*	6th head.
6850 ·0	5	*c*	7th head.
6852 ·5	5		
6883 ·8	4	*c*	8th head.
6919 ·4	4	*c*	9th head.
6951 ·8	2	*c*	10th head.
6988 ·8	2	*c*	11th head.
7054 ·5	10	*a*	1st head of 1st group.
7059 ·6	4	*b*	Sub-head.
7087 ·8	10	*a*	2nd head.
7092 ·9	4	*b*	Sub-head.
7125 ·5	10	*a*	3rd head.
7130 ·6	4	*b*	Sub-head.
7158 ·9	3	*a*	4th head ?
7197 ·7	2	*a*	5th head ?

Reference to Stellar Bands.

The use of greater dispersion has removed the doubt as to the agreement of the 7th group of flutings with Dunér's stellar band No. 4, to which reference was made in the former paper. It is now evident that the appearances described as "lines" near 5598, 5630, and 5662 are really the heads of short flutings of class *a*, as might have been suspected from the near equality of the intervals separating them from the weaker but more obvious flutings (when seen with small dispersion) at 5604, 5636, and 5668. This group, therefore, begins with the fluting at 5597·9, and there is no longer any uncertainty as to its general correspondence with the stellar band, for which Father Sidgreaves gives the wave-length 5597.

Evidence as to the presence in stars of the first group of titanium oxide flutings, beginning at 7054·5, is afforded by the recent photographs of the spectrum of Omicron Ceti taken by Mr. Slipher, of the Lowell Observatory.* It is stated that "the star spectrum stops so suddenly at λ 7040 as to leave little doubt that another of these bands begins at that point and outruns the sensitiveness of the plate into the red." There can be no doubt that the abrupt ending to which reference is made owes its origin to absorption by the 7054·5 group of titanium flutings. Still more recently, Mr. Newall has informed me that he has identified the three heads of the 7054·5 group in photographs of the spectrum of α Orionis.

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* 'Astrophysical Journal,' vol. 25, p. 236, April, 1907.

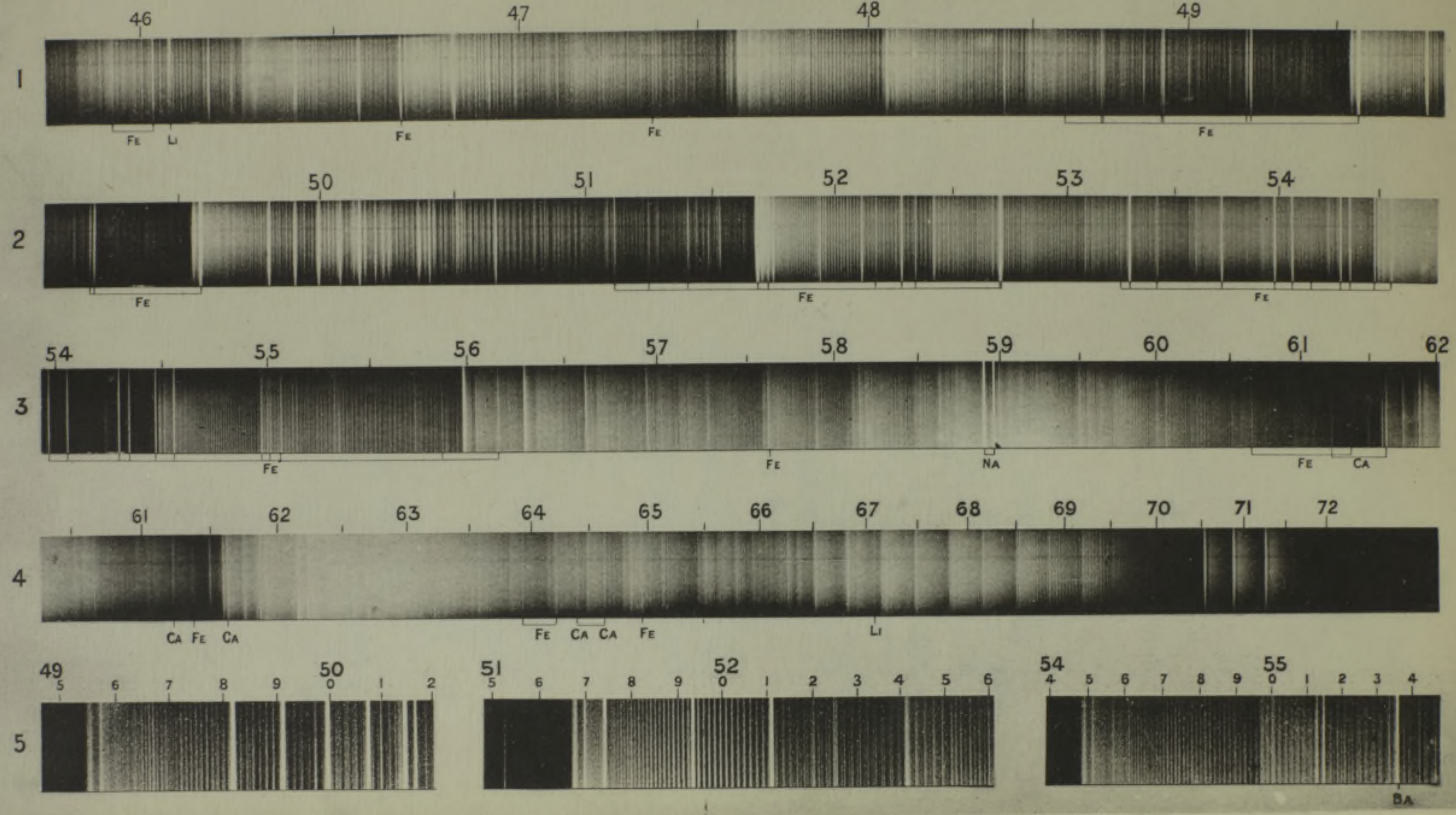
All the stronger groups of flutings have accordingly now been traced in stars, and it may be assumed that the fainter flutings of groups 3, 5, and 6 will also be present when the banded spectrum is well developed, as in α Herculis and o Ceti.

It still seems improbable, however, that titanium oxide can sufficiently account for all the stellar bands. As remarked in the former paper, the stellar intensities of Dunér's bands 1 and 3, beginning near 5862 and 6493, appear to be too great to be wholly accounted for by the titanium oxide flutings which occur in these parts of the spectrum. This is especially the case with the band at 5862, which is very frequently a wide and dark band in the stars, whereas the fluting at 5863·5 is an inconspicuous feature of the titanium oxide spectrum. The flutings in the neighbourhood of 6493 also seem to be too feebly marked in the titanium spectrum to produce a conspicuous absorption head in the stars. More accurate wave-lengths of the stellar bands in question are urgently required for further investigations of their origin.

The author is anxious to express his indebtedness for assistance rendered at different times by students in training assisting in the Astrophysical Department of the Royal College of Science. Valuable aid in carrying out the experiments described in the paper was given by F. W. Jordan, B.Sc., and J. Prescott, M.A., and the large-scale photographs were taken by H. Shaw, A.R.C.S., and E. J. Evans, B.Sc. The author is alone responsible for the determination of wave-lengths.

FLUTED SPECTRUM OF TITANIUM OXIDE.

(ARC-FLAME SPECTRUM OF TiO_2; 1–4, ON IRON POLES; 5, ON CARBON POLES)



The Spectrum of Scandium and its Relation to Solar Spectra.

By A. Fowler, A.R.C.S., F.R.A.S., Assistant Professor of Physics,
Imperial College of Science and Technology, South Kensington.

(Communicated by Sir William Crookes, D.Sc., F.R.S. Received June 23,—
Read June 25, 1908.)

(Abstract.)

The greater part of this investigation of the spectrum of scandium under different experimental conditions has been based on purified scandia, generously placed at the author's disposal by Sir William Crookes. The principal results are as follows:—

1. The arc spectrum of scandium consists of two distinct sets of lines, which behave very differently in solar spectra. Each set includes both strong and faint lines.

2. Lines belonging to one set correspond with the enhanced lines of other elements, notwithstanding that they appear strongly in the ordinary arc spectrum—

(*a*) These lines are very feeble or missing from the arc-flame spectrum, and are strengthened in passing to the arc, the arc in hydrogen, or the spark.
(*b*) They occur as relatively strong lines in the Fraunhofer spectrum.
(*c*) They are weakened in the sun-spot spectrum.
(*d*) They occur as high-level lines in the chromosphere.

3. The remaining lines show a great contrast when compared with the first group—

(*a*) They are relatively strong lines in the arc-flame.
(*b*) They are very feebly represented in the Fraunhofer spectrum.
(*c*) The stronger lines are prominent in the sun-spot spectrum.
(*d*) They have not been recorded in the spectrum of the chromosphere.

4. The special development of the enhanced lines in the Fraunhofer spectrum, together with their presence in the upper chromosphere, indicates that the greater part of the scandium absorption in the solar spectrum originates at a higher level than that at which the greater part of the iron absorption is produced.

5. The discussion of scandium lines indicates that while in the case of some elements solar identifications are to be based chiefly on arc lines, in

others it is the enhanced lines which may be expected to show the most important coincidences.

6. The flutings which occur in the arc and arc-flame do not appear when the arc is passed in an atmosphere of hydrogen. As suggested by Thalén, they are probably due to oxide of scandium.

Tables are given which show the lines of the arc spectrum from 3930 to 6580, the positions of the oxide flutings, and comparisons of the principal lines of the two classes with the sun, sun-spots, and chromosphere.

On the Vapour-pressure and Osmotic Pressure of a Volatile Solute.

By H. L. Callendar, M.A., F.R.S., Professor of Physics at the Imperial College of Science and Technology.

(Received June 17,—Read June 25, 1908.)

It follows by a method given in a recent paper by the author that if the osmotic membrane be assumed to be impermeable to the solute, the formula for the change of vapour-pressure of a volatile solute with hydrostatic pressure, and also the formula for the osmotic pressure which is deduced from it, must be the same as the formula for a non-volatile solute, and should not contain any terms depending on the vapour-pressure of the solute, except in so far as it may affect the hydrostatic pressure of the solution.

If, on the other hand, an osmotic membrane is regarded as a vapour-sieve, permeable to the vapour of the solution but not to the liquid phase, the equation takes a different form, depending on the concentration of the constituents in the vapour-phase. If c_1, c_2, etc., be the concentrations of the constituents in grammes per gramme of the vapour, and if U_1, U_2, etc., be the specific volumes of the constituents in the solution, the change of total vapour-pressure dp of the solution for a change of hydrostatic pressure dP is given by the relation,

$$\Sigma c\mathrm{U}\, d\mathrm{P} = v\, dp,$$

where v is the specific volume of the whole vapour-phase. If only one constituent is volatile, this relation reduces to the form $\mathrm{U}\, d\mathrm{P} = v\, dp$ for that constituent.

The Spectrum of Magnesium Hydride.

By Prof. A. Fowler, A.R.C.S., F.R.A.S.

(Communicated by Prof. H. L. Callendar, F.R.S. Received June 18,—Read June 24, 1909.)

(Abstract.)

The author has previously discovered that many of the band lines peculiar to the sun-spot spectrum are identical with lines composing the green fluting attributed to magnesium hydride by Liveing and Dewar. The present paper gives the results of a further investigation of this spectrum with high dispersion, together with details of wave-length determinations.

The principal results may be briefly summarised as follows:—(1) No sufficient reason has been found for modifying Liveing and Dewar's conclusion that the spectrum is produced by the combination of magnesium with hydrogen. (2) Lines are shown at short intervals in all parts of the spectrum from the extreme red to λ 2300, and definite groups of flutings begin at 5621·57, 5211·11, 4844·92, 4371·2, and near 2430. (3) From photographs of the magnesium arc in hydrogen at low pressures, taken with a 10-foot concave grating, the positions of close upon 2000 lines composing the three principal bands have been determined. The wave-lengths were derived from the interference standards of Fabry and Buisson, but have been corrected to Rowland's scale to facilitate comparison with solar spectra. (4) Twelve of the series of lines which compose the green band have been traced, and it is shown that none of the formulæ which have been proposed are sufficiently general in their application to represent all of these series within the limits of error of measurement. For the longer series the closest approximation is given by Halm's equation. (5) The identification of magnesium hydride in the sun-spot spectrum has been fully confirmed, and is clearly demonstrated by photographs submitted for reproduction. (6) It is shown that many of the bright interruptions of the dark background of the spot spectrum are not bright lines, but merely clear interspaces between lines or groups of lines in the spectrum of magnesium hydride. (7) The presence of the magnesium hydride flutings, together with flutings of titanium oxide and calcium hydride discovered at Mount Wilson, accords with the view that spots are regions of reduced temperature, and that their darkness is at least partly due to absorption. (8) The investigation of the possible presence of lines of magnesium hydride in the ordinary solar spectrum is for several reasons inconclusive, but there is evidence that very few, if any, of the thousands of faint lines tabulated by Rowland are to be accounted for by this substance.

Spectroscopic Investigations in connection with the Active Modification of Nitrogen.—I. Spectrum of the Afterglow.

By A. Fowler, F.R.S., Assistant Professor of Physics, Imperial College of Science and Technology, and the Hon. R. J. Strutt, M.A., F.R.S., Professor of Physics, Imperial College of Science and Technology, South Kensington.

(Received May 20,—Read May 25, 1911.)

[Plate 10.]

Method of Observation.

The method of producing and isolating the nitrogen afterglow adopted in the observations dealt with in the present paper was that described by one of us in the recent Bakerian lecture.* A continuous stream of nitrogen was passed at low pressure through the exciting discharge tube, from which it was drawn into a side tube which was viewed end-on through a quartz window. The source of nitrogen was the commercial compressed gas, but it was purified to the required degree by passage through a tube containing chips of phosphorus and other tubes containing caustic potash and phosphorus pentoxide. The purer the nitrogen the more brilliant was the luminosity of the afterglow; a small amount of oxygen in the nitrogen sufficed to destroy the deep yellow glow, and only a bluish-white luminosity was then visible.

Three spectrographs have been employed in the investigation; (1) a small quartz spectrograph, giving a linear dispersion of 5·5 cm. from λ 7000 to λ 2200; (2) a larger quartz spectrograph giving 11·5 cm. for the same extent of spectrum; (3) a Littrow spectrograph, with a prism of light flint glass, giving 16 cm. for the region λ 7000 to λ 3800. For the determination of wave-lengths, comparison spectra of copper (with impurities of lead, etc.) were chiefly used.

General Description of the Spectrum.

As seen and photographed with instruments of small dispersion, the spectrum of the afterglow produced by the above method appears to be identical with that described by Lewis.† The luminosity, however, is so great, and its maintenance so easy, that considerable dispersion may be employed, and long exposures given, so that the spectrum can now be examined in much greater detail.

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* R. J. Strutt, 'Roy. Soc. Proc.,' 1911, vol. 85, p. 219.

† 'Astrophys. Journ.,' 1904, vol. 20, p. 49.

The spectrum may be conveniently considered to consist of three groups of bands, namely :—

Group α.—Three very conspicuous bands in the red, yellow, and green, with the brightest parts about wave-lengths 6252, 5804, and 5407. Another faint band about 5054 also belongs to this group.

Group β.—A series of 11 bands in the violet and ultra-violet, extending from 4312 to 2503. These are degraded towards the red, and have double heads. Other fainter series of bands of similar structure also belong to this group.

Group γ.—A series of flutings, degraded to the more refrangible side, corresponding in every particular with Deslandres' "third positive" group of nitrogen bands. These have double-double heads and extend from 3009 to 2155.

The stronger members of the second positive group of nitrogen bands (degraded to the violet, and extending from about 5000 to 3000) also appear in the spectrum of the afterglow, but they may have been introduced by internal reflections of the light from the exciting discharge tube, or by stray discharges in the afterglow tube itself, as Lewis did not find them by his method of observing the afterglow only when the discharge was interrupted. The first head of the cyanogen band at 3883 was also frequently present, but it may be accounted for by a slight carbon impurity,* and is not to be regarded as a part of the afterglow spectrum of pure nitrogen. The presence of carbon compounds was sometimes shown in another way by the strong line of carbon at 2478·7 in the spectrum of the discharge tube when the condenser was in circuit.

The Bands of Group α.

The three bands of group α, in the less refrangible part of the visible spectrum, are the most striking feature of the afterglow spectrum when the nitrogen is as pure as possible. Their true characters and relationships were not revealed until they were photographed with the comparatively great dispersion of the Littrow spectrograph. It was then found that their structure was identical with that of the "first positive" bands of nitrogen, and further investigation revealed the previously unsuspected fact that they are also identical in position with bands of nitrogen. This result is shown by the photographic comparison given in Plate 10, fig. 1, which indicates the extraordinary selection of first positive bands for special enhancement in the afterglow. It will be seen that the afterglow bands are not merely a survival of the brightest of the first positive bands,* but represent a special development of the more refrangible parts of the three groups into which the first positive spectrum is visibly divided.

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* See Strutt, *loc. cit.*, p. 228.

The positions of the various bands are roughly shown by the wave-length scale marked on the photographs. Adopting Von Helm's values for the nitrogen bands,† the wave-lengths and oscillation frequencies of the first heads of the principal bands which occur in the afterglow spectrum are as indicated in Table I.

Table I.—The Visual Bands of the Afterglow (Group α).

Wave-length.		Intensity.	Frequency *in vacuo.*	Frequency difference.	Second difference.
Red ...	6322 ·73	2	15812		
	6252 ·81	5	15989	1235	
	6185 ·44	1	16163		
Yellow	5854 ·69	4	17076		
	5804 ·28	10	17224	1265	30
	5755 ·20	8	17371		
Green	5442 ·25	1	18370		
	5407 ·08	5	18489	1293	28
	5372 ·78	5	18607		
Green	5053 ·6*	2	19782		
	5030 ·8*	2	19872		

* Measures by Hasselberg. Identified by visual observations.

The frequency differences and second differences for the strongest heads of the bands are given in the fourth and fifth columns of the table, and similar figures are obtained for the other corresponding heads. These differences are of interest as showing that the afterglow bands have not been selected at random from the numerous series which build up the first positive spectrum of nitrogen, but that they constitute three definite series of the usual character. They are, in fact, identical with three consecutive horizontal series in Cuthbertson's arrangement of the first positive bands of nitrogen in 13 series,‡ namely:—

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* The faint bands less refrangible than 6322 shown in the photograph probably do not form part of the true afterglow spectrum, but represent part of the normal first positive spectrum accidentally superposed on that of the afterglow.

† Kayser's 'Handb. der Spectroscopie,' vol. 5, p. 828.

‡ 'Phil. Mag.,' 1902, [6], vol. 3, p. 348.

	Series 3.	Series 4.	Series 5.	Series 6.	Series 7.
Series α_1 ………	18370	17076	15812		
	1412	1413	1412		
Series α_2 ………	19782	18489	17224	15989	
		1383	1383	1382	
Series α_3 ………		19872	18607	17371	16163

The association of the bands in the afterglow suggests that of the various possible arrangements of the first positive bands the horizontal series in the above table are perhaps specially significant. It will be observed that, on the frequency scale, a displacement of one of the horizontal series by an appropriate amount will result in its superposition on one or other of the remaining series, thus resembling the five series into which the second positive bands of nitrogen have been divided by Deslandres.*

The relation between the bands is shown in another way by the application of Deslandres' general formula for the first positive bands,† namely :—

$$n = 22785{\cdot}1 - \frac{30{\cdot}319}{8}(2m)^2 + \frac{29{\cdot}363}{8}(2p+1)^2.$$

The first horizontal series of the above table is obtained when $m = 47$ and $p = 42, 43, 44$; the second when $m = 46$ and $p = 41, 42, 43, 44$; and the third when $m = 45$ and $p = 40, 41, 42, 43$. The bands shown in fig. 1*b* which are less refrangible than 6322 do not belong to either of these series, and, as already pointed out, they probably do not form part of the afterglow spectrum, but have been introduced by accident.

It thus appears that, in the less refrangible part of the spectrum, the afterglow shows no new bands, and only differs from that of the ordinary discharge through nitrogen in the concentration of the luminous energy into a small selection of the numerous series into which the first positive spectrum can be divided.

It should be noted also that the first positive bands of nitrogen are greatly reduced in intensity in the condensed discharge, which generates the afterglow, as compared with the uncondensed discharge, so that the partly abolished first positive bands may be considered to reappear in the afterglow, but with greatly modified intensities. Apart from the modification of intensities, for which we can offer no explanation at present, this observation is in accordance with the view that nitrogen is partially dissociated in the condensed discharge, and that the afterglow is produced during the re-formation of ordinary nitrogen.

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* 'Comptes Rendus,' 1887, vol. 104, p. 972.

† 'Comptes Rendus,' 1902, vol. 134, p. 747.

The Bands of Group β.

The general character of the second group of bands, designated the β group, will be gathered from Plate 10, fig. 2*b*. The positions of the brighter bands were only very roughly determined by Lewis, and it has been thought desirable to determine them with the considerable accuracy which is made possible by the use of the larger quartz spectrograph, and to include as many as possible of the fainter bands for the investigation of series relationships. The resulting wave-lengths for the principal series of bands, and their approximate intensities on a scale of 10 for the strongest, are shown in Table II, together with the oscillation frequencies *in vacuo*, and the first and second differences. The analysis of the intervals separating the bands suggests that the wave-lengths are correct to a few tenths of a tenth-metre.

Table II.—Group β Bands of the Afterglow.

Wave-length.	Intensity.	Frequency *in vacuo*.	Frequency difference.	Second difference.
4312·3 4296·5	1	23183 23268		
			1547	
4042·8 4028·7	2	24728 24815		21
			1568	
3801·9 3789·3	4	26295 26383		30
			1598	
3584·7 3572·9	6	27888 27981		26
			1624	
3387·2 3376·8	9	29514 29605		28
			1652	
3207·4 3198·4	10	31169 31257		31
			1683	
3043·2 3035·0	10	32851 32940		24
			1707	
2893·0 2885·4	9	34556 34647		27
			1734	
2754·5 2747·9	7	36294 36381		29
			1763	
2626·9 2620·9	4	38057 38144		30
			1793	
2509·0 2503·2	1	39845 39937		

It will be seen that the bands form a well-defined series, with the strongest bands about the middle, as is often the case with band spectra.

The average second difference is about equal to that which appears to be common to the first and second positive nitrogen series, but otherwise the series is quite distinct, and the bands have a structure which is different from that of any of the other bands attributed to nitrogen.

The oscillation frequencies of the more refrangible heads of the bands are closely represented by the formula

$$n = 13{\cdot}89\, m^2 - 18747,$$

where m has values ranging from 55 to 65. The calculated differ from the observed values by amounts which only once reach as much as three units.

In addition to this chief series of bands, there are several fainter ones of similar structure, particulars of which are given in Table III (see also Plate 10, figs. 2*b* and 3*b*). These also form series, which may be conveniently designated β_1, β_2, etc., as in the last column of the table. The intensities are roughly on the same scale as those of the main series in the previous table.

Table III.—Fainter Bands of Group β.

Wave-length.	Intensity.	Frequency *in vacuo.*	Series.	Wave-length.	Intensity.	Frequency *in vacuo.*	Series.
2951·2 2944·0	2	33875 33958	β_1	2558·0 2552·3	2	39082 39169	β_1
2923·8 2916·2	2	34192 34281	β_3	2542·8 2537·1*	1	39315 39404	β_3
2809·7 2802·7	2	35581 35670	1	2493·9 2488·3	3	40086 40176	β_2
2786·5 2780·1	2	35877 35960	β_3	2433·2 2428·2	3	41086 41171	β_3
2732·2 2726·0	1	36590 36673	β_2	2387·0 2382·3	1	41881 41964	β_2
2678·8 2672·9	3	37319 37402	β_1	2331·5 2326·8	2	42878 42965	β_3
2608·6 2602·9	2	38324 38408	β_2	2236·1 2232·3	1	44707 44783	β_3

* This head is hidden by the mercury line 2536·7, accidentally present, and its position has been estimated by consideration of the intervals separating the component heads.

These secondary series are related to the chief series and to each other in the same way that the constituent series of the first or second positive groups are related, such that a general displacement of one series by the proper amount will superpose it upon one of the other series. This is shown in the following arrangement of the frequencies:—

	$m = 66$.	$m = 65$.	$m = 64$.	$m = 63$.	$m = 62$.	$m = 61$.	$m = 60$.
Series β ...		39937	38144	36381	34647	32940	31257
			1025	1021	1023	1018	
,, β_1 ...			39169	37402	35670	33958	
			1007	1006	1003		
,, β_2 ...		41966	40176	38408	36673		
		999	995	996			
,, β_3 ...	44783	42965	41171	39404		35960	34281

It follows that the formula for the main series may be adapted to the secondary series by an alteration of one of the constants thus—

$$\text{Series } \beta_1 \ldots\ldots\ldots \quad n = 13{\cdot}89\,m^2 - 17725.$$
$$,, \quad \beta_2 \ldots\ldots\ldots \quad n = 13{\cdot}89\,m^2 - 16718.$$
$$,, \quad \beta_3 \ldots\ldots\ldots \quad n = 13{\cdot}89\,m^2 - 15723.$$

The values of m for the several vertical columns are shown in the tabular arrangement above. Series β_3 fails to show the band corresponding to $m = 62$ (λ 2653·8), although there is no other band at this place which could mask it.

The several series of group β must clearly be regarded as forming a connected system, but they have no evident relation to the other known series of nitrogen bands. As in the case of the α group, however, the β group does not represent a spectrum which exists exclusively in the afterglow. The stronger bands were observed faintly by Lewis in the ordinary discharge through nitric oxide, and our own experiments have indicated that they occur under suitable conditions in similar discharges through air or nitrogen. This is illustrated in the case of air in Plate 10, fig. 2a. The original negatives show the five strongest bands of group β (3377 to 2748) and the four bands of the series β_2, and it is remarkable that the latter are relatively more developed than the chief β series in the air discharge.

The bands of group β are found in association with the third positive bands of nitrogen, dealt with in the next section, and, as in the case of those bands, we have not found sufficient evidence to show that anything but nitrogen is necessary for their development.

The general result of the investigation of the β group of bands is to show that, like group α, they tend to disappear from the spectrum of the exciting discharge, and they reappear with somewhat modified intensities in the afterglow.

The Bands of Group γ.

As already remarked, the third group of afterglow bands is identical with the third positive band spectrum of nitrogen. This is indicated by the photographs reproduced in Plate 10, fig. 3, which show the spectrum of the afterglow in comparison with that of air. For convenience of reference, the positions of the less refrangible heads, from the data given by Schniederjost,[*] are indicated in Table IV.

Table IV.—Chief Heads of Third Positive Bands of Nitrogen.

3009·55	2478·90
2859·80	2370·38
2722·43	2269·57
2595·80	2154·80

These bands occur strongly in several other sources besides the afterglow and the uncondensed discharge in air or nitrogen. They are found in the spectrum of an uncondensed spark in air at atmospheric pressure, in the arc between metallic poles, in the flame of cyanogen, and in the flame of ammonia burning in oxygen. Deslandres has suggested that they may be due to an oxide of nitrogen—developed by traces of oxygen in the case of a supposed nitrogen tube—as he found them to disappear from the spectrum when the nitrogen had been passed over heated sodium. The absence of the bands from the *condensed* discharge in nitrogen is also regarded by Lewis as favouring their oxide origin, the idea being that the bands vanish because of the decomposition of the compound which is thought to produce them.

We have not been able to convince ourselves, however, that these third positive bands require anything more than nitrogen for their production. With all precautions to exclude oxygen, the bands have always been present in the afterglow spectrum, even when the nitrogen was passed through melted phosphorus before it entered the discharge tube. In the discharge tube itself, it was found that the presence or absence of the bands seemed to depend only upon the intensity of the discharge. In the condensed discharge, and in the uncondensed discharge, if of sufficient intensity, the bands in question are wanting, but with other things remaining the same they made their appearance when the strength of the discharge was sufficiently reduced. It would thus appear that the third positive bands are more sensitive to changes in the discharge than the bands of the first and second positive groups, and are the first to be abolished as the discharge approaches that necessary to produce the line spectrum.

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[*] 'Zeitsch. f. wiss. Photog.,' 1904, vol. 2, p. 265.

The general behaviour of these bands in relation to the afterglow is very similar to that of the α and β groups. They occur in the uncondensed discharge, disappear in the stronger discharge which produces the afterglow, and reappear in the afterglow; they differ from the other two groups, however, in that there is no notable change in the relative intensities of the component bands.

Spectrum of Exciting Discharge.

It seemed important to compare the spectrum of the condensed discharge which develops the afterglow with that of the uncondensed discharge which ordinarily fails to do so. In the first place it was found that a discharge giving only the line spectrum does not excite the afterglow. A special tube was constructed with a very narrow capillary. The electrodes projected almost into this capillary, so as to avoid any development of the band spectrum in the wider parts of the tube, which might have made the result ambiguous. A current of pure nitrogen was passed through this tube, excited by the condensed discharge, but no afterglow was observed. The same current of rarefied nitrogen passed on its way to the pump through a wider discharge tube capable of giving the band spectrum. When the discharge was transferred to this tube, the afterglow was well developed. This served as a check, to prove that the failure to obtain the afterglow in the previous instance had not been due to any defect in the quality of the gas. It was accordingly only necessary to investigate the modifications of the *band* spectrum which occur in passing from a discharge of moderate intensity without condenser to a discharge with the condenser.

It was already known that the effect of the condenser is to reduce the intensity of the first positive bands, to brighten the second positive bands, and to abolish those of the third positive group. We have found in addition that a new series of seven bands in the ultra-violet appears in the spectrum of the condensed discharge. There appears to be no previous record of these bands in the observations made by Deslandres and others, but there seems to be no reason to doubt that they belong to nitrogen. For purposes of reference, this series may be conveniently called the "fourth positive" group of nitrogen.

As photographed with the larger quartz spectrograph (Plate 10, fig. 4*b*), each of the fourth positive bands shows five principal heads, of which the most refrangible is the strongest in each case, and the middle one next in order of brightness. The flutings are degraded towards the more refrangible end of the spectrum.

The wave-lengths of the bands, their relative intensities, oscillation frequencies, and frequency differences are shown in Table V.

Table V.—Fourth Positive Bands of Nitrogen.

Wave-length.	Intensity.	Frequency *in vacuo.*	Frequency difference.	Second difference.	Remarks.
2903·9		34427			
02·0		449			
00·3	1	469			
2898·1		496	1561		
96·6		34513			
2777·9		35988		27	
76·5		36006			
75·1	2	024			Also a faint head at 2774·3.
72·8		054	1588		
71·4		36072			
2660·5		37576		28	
59·3		593			
57·9	5	613			Also a faint head at 2657·0.
55·8		643	1616		
54·5		37661			
2550·7		39192		30	
49·7		209			
48·4	8	229			
46·6		257	1646		Also a faint head at 2547·7.
45·3		39277			
2448·0		40838		31	
47·0		854			
45·6	10	878			Also a faint head at 2445·0.
44·0		905	1677		
42·8		40925			
2351·4		42515		27	
50·3		535			
49·0	6	559			
47·5		586	1704		
46·4		42606			
2260·8		44219			
59·6		242			
58·4	2	266			This band is not very well defined on the photographs.
57·1		291			
56·0		44313			

The structure of these bands is different from that of any belonging to the other groups of nitrogen, but a possible relation to the second positive bands is suggested by a consideration of their series relationships, and by the fact that both sets of bands are specially developed in the condensed discharge. The probable relation of the new bands to the second positive nitrogen group will be sufficiently indicated by the following comparison with Series III of the second positive spectrum. The oscillation frequencies (*in vacuo*) for the latter have been calculated from the wave-lengths given by Ames* :—

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* 'Phil. Mag.,' 1890, [5], vol. 30, p. 48.

2nd positive. Series III.	4th positive. First heads.	Difference.
23798	34427	10629
25357	35988	10631
26946	37576	10630
28562	39192	10630
30208	40838	10630
31882	42515	10633
33585	44219	10634

The difference is constant within the limits of error, and numerically, at least, the fourth positive bands are related to the second positive as the several series of the latter are related to each other. The figures in the first and second columns of the foregoing table may be respectively calculated from the formulæ

$$n = 14{\cdot}306\,m^2 - 17918,$$
$$n = 14{\cdot}306\,m^2 - 7288,$$

where m ranges from 54 to 60.

The fourth positive bands appear to be the most characteristic feature of the spectrum of the discharge which produces the afterglow, but a change of state in the nitrogen is also indicated by the modified intensities of the other three positive groups. The bands are also found, but with less intensity, in the condensed discharge through a tube containing air, and if they are characteristic of the afterglow-producing gas, it may be presumed, in accordance with other experiments, that the absence of the nitrogen afterglow in air tubes is due to the presence of oxygen.

Summary.

(1) The paper gives a detailed account of the spectrum of the afterglow of pure nitrogen, with wave-length determinations of sufficient accuracy to indicate the series relationships of the various bands.

(2) The characteristic bands of the afterglow in the red, yellow, and green are complex groups which have been found to be identical with some of the bands forming the sequence known as the first positive group of nitrogen. They represent a special development of three of the numerous series into which the first positive bands have been divided.

(3) The second group of afterglow bands, extending from 4312 to 2503, corresponds with a group of faint bands which occur in the uncondensed discharge in air or nitrogen, and the third group is identical with the third positive group of nitrogen bands, as previously shown by Lewis.

(4) The most characteristic feature of the condensed discharge which

produces the afterglow is a series of seven complex bands, occupying the region 2904 to 2256, which have not previously been recorded as belonging to nitrogen. It is suggested that these should be designated the "fourth positive" group of nitrogen bands.

(5) No afterglow is excited when the discharge is such as to give only the line spectrum of nitrogen.

The authors are indebted to Mr. H. Shaw, A.R.C.S., for valuable assistance in the computation of wave-lengths, and in enlarging the photographs for reproduction.

DESCRIPTION OF PLATE.

1*a*. Uncondensed discharge in nitrogen, showing the first positive bands in the red, yellow, and green.

1*b*. Afterglow bands of Group *a*, showing relation to first positive bands.

2*a*. Uncondensed discharge in air, violet and ultra-violet region, showing second positive bands of nitrogen, part of the third positive group, etc.

2*b*. Afterglow bands of Group β, which are also seen faintly in the spectrum of air, 2*a*.

3*a*. Uncondensed discharge in air, ultra-violet region, showing the third positive bands of nitrogen, etc.

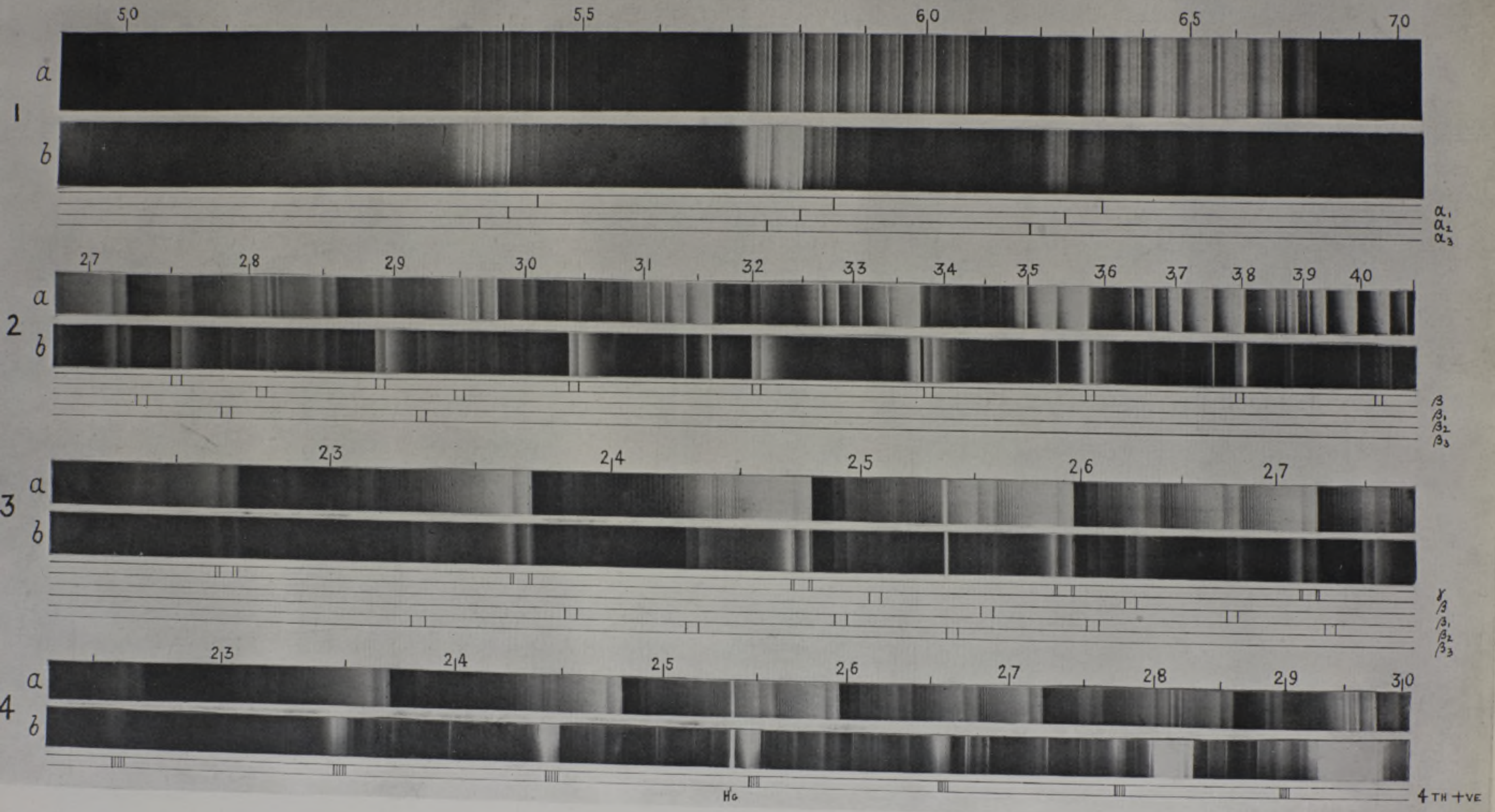
3*b*. Afterglow bands of Group β and Group γ (third positive nitrogen).

4*a*. Uncondensed discharge in nitrogen, ultra-violet region.

4*b*. Condensed discharge in nitrogen, which excites the afterglow, showing the new "fourth positive" bands.

1*a* and 1*b* were taken with the Littrow spectrograph and the remainder with the larger quartz spectrograph. The scales attached to the photographs are strictly only applicable to the upper spectrum in each pair, owing to difficulties of mounting.

SPECTRUM OF NITROGEN AFTERGLOW



of electricity divided by the mass of the hydrogen atom it should be about 9660.

The model has thus been tested numerically on three independent points. It gives 2·32 for the ratio of the wave-lengths instead of 2·00, and it gives 7110 or 1550 for the value of e/m instead of 9660, according as we use the first or second band. If we consider the simplicity of the assumptions made, and the room there is for modification (*e.g.* making k different for the different linkings), the agreement must be regarded as gratifying.

The other maxima in the absorption spectrum are possibly due to more complex molecules.

This is incidentally the first time that chemical bonds have been connected mathematically with absorption bands.

Spectroscopic Investigations in Connection with the Active Modification of Nitrogen. II.—*Spectra of Elements and Compounds excited by the Nitrogen.*

By the Hon. R. J. Strutt, M.A., F.R.S., Professor of Physics, and A. Fowler, F.R.S., Assistant Professor of Physics, Imperial College of Science and Technology, South Kensington.

(Received November 13,—Read November 23, 1911.)

[Plate 6.]

Introductory.

In continuation of previous accounts of the active modification of nitrogen,* and of the spectrum of the afterglow which is associated with it,† the present paper gives further details of the spectra which are developed when various elements and compounds are introduced into the glowing gas. Preliminary investigations of the spectra were made by direct observation, and with a small quartz spectrograph, and when greater resolving power was required a larger quartz spectrograph and an instrument of the Littrow type were used.

The arrangements for producing the afterglow were as described in the previous papers. By means of a mechanical pump a stream of purified nitrogen at low pressure was passed through the discharge tube, and the afterglow was observed in a side tube, into which the various substances were introduced as required. It will be remembered that a discharge with condenser and spark gap is necessary to develop the afterglow with maximum intensity.

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* R. J. Strutt, Bakerian Lecture, 'Roy. Soc. Proc.,' 1911, A, vol. 85, p. 219.

† A. Fowler and R. J. Strutt, 'Roy. Soc. Proc.,' 1911, A, vol. 85, p. 377.

Later experiments have shown that the afterglow is also generated by the ring discharge produced by electromagnetic induction when the pressure of the nitrogen is appropriately adjusted. The spectrum of the exciting discharge is identical with that of the condensed discharge which has already been described; that is, the first positive bands of nitrogen are feeble, the second positive bands very intense (giving a bluish colour to the ring), the third positive group absent, and the fourth positive bands present.

We mentioned in our previous paper (p. 377) that the deep yellow afterglow was destroyed by a small amount of oxygen in the nitrogen employed, and that only a bluish-white luminosity was then visible. This is due, as we have since ascertained, to the formation of a small quantity of nitric oxide by combination of oxygen and nitrogen in the discharge; for the same effect is produced if a very small quantity of ready made nitric oxide is introduced into the stream *after* it has passed the discharge tube. Larger quantities introduce a different phenomenon—the yellow-green flame with continuous spectrum.* The effect of a small nitric oxide admixture is to suppress the α-group of afterglow bands, leaving the rest of the afterglow spectrum untouched.

Metallic Elements.

Sodium.—It has already been pointed out by one of us that when sodium is heated a little above its melting point in the presence of active nitrogen, the sodium spectrum is developed with great brilliancy; when heated more strongly, the vapour close to the metal becomes visibly green, and in this region the D lines almost vanish, while the pair of green lines about 5685† is shown very strongly. Other lines of the subordinate series are also very bright, and lines of potassium appear as impurities.

As regards the principal series, the photographs suggest that the suppression of the D lines does not so much indicate a tendency towards the extinction of this series as a change in the position of maximum intensity to the next pair of lines in the series near 3303, which is the strongest in the whole spectrum; other lines of the principal series at 2853 and 2680 are also well visible.

In the first subordinate series the greatest intensity is towards the red end, and the colour of the glowing vapour indicates that the maximum occurs at the green pair 5685. The second subordinate series is relatively very weak. Apart from the redistribution of intensity in the principal series, however, the spectrum approximates very closely to that given by sodium in the oxy-hydrogen flame or electric arc.

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* R. J. Strutt, 'Roy. Soc. Proc.,' in course of publication.

† Wrongly referred to in the Bakerian Lecture as the E line.

The suppression of the D lines recalls an experiment described many years ago by Lockyer,* in which a similar result was obtained. In this case an electric discharge was passed through a capillary tube which was in connection with a wider tube containing heated metallic sodium, the platinum electrode nearest to the metal being a few inches above it. There was no obstruction between the electrode and the sodium, and the only gas present was the hydrogen given off by the metal.

The similar results obtained in hydrogen and nitrogen suggested that in both cases the effect might be due to the production of the spectrum under reduced pressure. We have not, however, been able to produce the same phenomenon by passing a discharge through sodium vapour in a vacuum tube, although the lines of the subordinate series were well displayed under these conditions.

Potassium.—The photographed spectrum was rather faint, but it showed very clearly the lines of the principal series at 4046, 3447, 3217, and 3102, the first named being by far the strongest. Several lines belonging to the two subordinate series were shown faintly, and there were feeble indications of a band fading to the violet, with its head about 460.

Magnesium.—The spectrum of this metal was only observed with difficulty, and the photograph obtained was not very strong. Nevertheless it sufficed to show that the spectrum did not contain any of the characteristic spark lines, such as that at 4481·3. The characteristic flame line at 4571 appeared faintly, while the adjacent line at 4703, which is a much stronger line in the arc spectrum, did not appear. The spectrum thus approximates closely to that given by the flame, but it tends to be intermediate between the flame and the arc. The lines photographed are shown in the following table :—

Wave-length.	Intensity in glow.	Remarks.
4571·33	1	Characteristic flame line.
3838·44	10	1st line of triplet, 1st subordinate series.
3336·83	1	,, ,, 2nd ,, ,,
3097·06	3	,, ,, 1st ,, ,,
2852·22	2	,, ,, 1st ,, ,,
2779·94	3	Arc line, not included in series.

The *b* group was observed visually, but was not photographed.

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* 'Roy. Soc. Proc.,' 1879, vol. 29, p. 266.

Mercury.—The mercury line spectrum is well developed in active nitrogen, and the photograph shows all the stronger lines of the arc spectrum which are given by Kayser and Runge. With the exception of the pair 5790, 5769, and the line 4078, all the lines photographed belong to the two triplet series, and include numbers 4 and 5 of the first subordinate series, and numbers 3 and 4 of the second subordinate series. The relative intensities of the lines are not notably different from those of the arc spectrum. Comparisons with the spectrum of a mercury lamp revealed no distinct difference.

Thallium.—The chloride of the metal was employed in this experiment, but no bands special to the compound were observed or photographed. The glow produced was bright green, and the spectrum consisted of numerous sharply defined lines. With the exception of two probable impurity-lines at 3239, 3220, the lines agree very closely with those of the arc spectrum, as regards their relative intensities, but there are indications that the second subordinate series is somewhat weaker than in the arc.

Nickel.—Nickel chloride was used, but the only bands observed were afterwards found to be identical with those given by cuprous chloride, and they may therefore be referred to an impurity of copper in the substance employed. Some of the lines of copper were also shown in the photographs. In addition, between 20 and 30 lines due to nickel itself were photographed, and these are identical with the strongest arc lines of the metal, so far as they can be identified with the small dispersion employed. The lines were most distinct in the ultra-violet region, 3620 to 2900, where there were no copper bands to mask them.

The Halogens.

Iodine.—The vapour given off by iodine at ordinary temperatures readily generates a characteristic bright blue glow when it comes in contact with active nitrogen. The spectrum shows a broad faint band in the green, and a number of ill-defined bands in the blue and ultra-violet, of which one at about 3430 is by far the most prominent (Plate 6, fig. 1). In addition, there is an apparently continuous background, which is feeble on the less refrangible side of a band at 4770, but is quite strong from that wave-length to the most refrangible part of the spectrum shown on the photographs. The bands as a whole do not appear to have been previously recorded, but the strongest band has been noted by Könen,* who describes it as extending from 3430 to 3340. We have found, however, that the vacuum tube shows all the bands of the glow spectrum in the region compared (3200 to 5900), but the vacuum tube differs from the glow in showing greater luminosity in the less refrangible parts of the spectrum. Also, while the most intense band in the vacuum-tube is at 4310, that in the glow is at 3430. Details relating to the bands of the glow spectrum are given in the appended table.

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* 'Wied. Ann.,' 1898, vol. 65, p. 269.

Wave-lengths of Iodine Bands.

Approx. wave-length.	Intensity.	Approx. wave-length.	Intensity.
4770	5	2890	3
4620	3	2835	2
4310	5	2775	2
3890	2	2720	1
3535	1	2480	2
3495	1	2430	1
3430	10	2380	1
3270	2	2075	5

The last on the list, at 2075, is a strong sharp line, quite unlike the others in appearance, but there seems to be no reason to assign it to any impurity, as it has not been found in mercury or any other substance likely to be present.

The band at 4770 was photographed with the Littrow spectrograph, but there were no signs of resolution into fine lines in a spectrum of purity 3000 in that region.

It should be noted that the flutings shown in fig. 1, which only occupy the upper half of the spectrum, are due to nitrogen.

Bromine.—The luminosity in this case was very feeble, and the photograph of the spectrum shows only one band which can be attributed to bromine. This is a broad symmetrical band, having ill-defined edges about 2930 and 2890. A band in the orange, dominating the colour of the glow, was observed visually.

[*Note added December* 5.—This band is not identical with the yellow-green band recorded in the vacuum tube spectrum by Eder and Valenta. With moderate dispersion it was found to consist of eight narrow bands extending from about 5875 to 6070, at nearly equal distances of 28 tenth-metres.]

Lines of aluminium were well seen in this spectrum, the metal having been carried forward into the glowing gas, probably in the form of a volatile bromide.

Chlorine.—The spectrum of chlorine excited by active nitrogen was similar to that of bromine, but the single broad band shown on the photograph occurs in a more refrangible part of the spectrum, namely, 2600 to 2540. No lines of chlorine were recorded on the photograph.

Compounds of Metals.

Cuprous Chloride.—The blue-green glow developed by cuprous chloride gives a spectrum which is generally similar to that of the same substance when volatilised in the Bunsen flame. The afterglow, however, produces a greater number of lines of copper, and the band spectrum of the chloride is more completely developed. The chloride bands are also better visible in the glow than in the flame, in consequence of the absence of overlying continuous spectrum. A series of bands which is either absent from the flame, or is very weak, is a conspicuous feature in the glow spectrum. These bands are more refrangible than those which occur in the flame, their approximate wave-lengths being 4150, 4080, 4010, 3945, 3885, 3835, 3785, 3740. The intervals between the bands suggest that they form a connected series which is related to those in which the flame bands have been arranged by Kien.*

Chlorides of Tin.—Stannous and stannic chlorides produce a brilliant blue glow. The most striking feature shown on a photograph of the spectrum of stannic chloride is an intense band in the blue, extending from about 4000 to 5000; with small dispersion, the band shows no signs of any maxima, and fades off gradually in both directions (Plate 6, fig. 2). In addition there are seven lines of tin between 3262 and 2706, which are identical with the strongest lines of the arc spectrum in this region. There are other faint lines at the approximate positions 3855, 3780, 3748, 3480, and 3474, which have not yet been identified.

A photograph of the blue band, taken with the Littrow spectrograph, shows that it is not perfectly continuous. Superposed on the continuous background, there are several symmetrical but ill-defined bands, 4 or 5 tenth-metres broad, which show no further signs of resolution in a spectrum of a purity of about 4000 in the region where the bands occur. Accurate measures of these bands cannot be obtained, and it will suffice to state that there are 15 bands between 4768 and 4430, at nearly equal distances of 24 tenth-metres. Some of the bands are double. The bands are very similar in appearance to those which occur in fluorescence spectra, as, for example, that of uranium phosphate. An experiment was accordingly made in order to ascertain if a fluorescence could be obtained by the action of ultra-violet light on stannic chloride.

A small quantity of stannic chloride was placed in a quartz tube, 2 cm. in diameter, which was exhausted and sealed, the liquid chloride being frozen with liquid air during this operation. The quartz tube was then examined in a concentrated beam from an electric lantern with quartz condensers, with and without a deep violet glass. But no fluorescence could be observed, either at the ordinary temperature or when the tube was warmed.

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* 'Zeit. für Wiss. Photog.,' 1908, vol. 6, p. 337.

Experiments on the vacuum-tube discharge through the vapour of stannic chloride showed that the discharge was generally similar in colour to the glow produced in active nitrogen, but was not so perfect a blue. The vacuum-tube spectrum, however, showed the same strong blue band as the glow, but there was also a fairly bright continuous, or nearly continuous, spectrum extending from the blue band to the red. Lines of tin were also more prominent in the vacuum-tube than in the glow.

Mercuric Iodide.—This substance yields a violet glow, and the spectrum shows bands which appear to be characteristic of the compound, together with a feeble band which coincides with the principal band of iodine about 3430. Mercury was only represented by the line 2536·7, which was no stronger than in other spectra obtained in the same manner when mercury was only accidentally present.

The strongest band begins at about 4455. It is very intense from that point to 4390, after which it fades off rather rapidly to the neighbourhood of 3700. With the small resolving power employed, the band is a nearly continuous one, but there are indications of numerous ill-defined maxima. The spectrum, as a whole, is similar to that described by Jones,* and afterwards by Lohmeyer,† as occurring in mercuric iodide rendered luminous in a vacuum tube. For the brightest band the wave-length of the beginning is given by Jones as 4396, but from the description there can be no doubt that it is the same band as that found in the glow. Lohmeyer's wave-lengths, giving the brightest parts of the band as lying between 4456 and 4393, confirm this. The remaining (faint) bands agree with those tabulated by Jones.

Sulphur and its Compounds.

Sulphur.—When sufficiently heated in the glowing nitrogen, sulphur gives a blue glow. The spectrum consists of a succession of bands, degraded to the red, and very evenly distributed. Between 4700 and 2800 there are about 30 principal bands, some of which are complex groups or doublets. There was little or no continuous spectrum. The spectrum has nothing in common with that of sulphur in a vacuum tube, but it is closely related to that given by the flame of carbon disulphide burning in air. In the flame, however, the bands are superposed on a moderately strong continuous spectrum, and those which are more refrangible than 3400 are only very feebly displayed.* When the flame was supported by oxygen, it was found that the bands were barely visible, while another group in the region 3000 to 3200 (seen also in the flame of burning sulphur) was introduced.

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* 'Ann. d. Physik.,' 1897, vol. 42, p. 50.

† 'Zeit. für Wiss. Photog.,' vol. 4, p. 376.

Sulphuretted Hydrogen.—The spectrum obtained when sulphuretted hydrogen was introduced into active nitrogen was identical with that given by sulphur in the nitrogen.

Carbon Disulphide.—The spectrum given by carbon disulphide in nitrogen showed the bands already described as occurring with sulphur, but the bands were only well developed on the less refrangible side of 3700. The cyanogen band 3883 and the carbon line 2478 were shown feebly.

In the ultra-violet there was an additional series of well-marked bands, degraded to the red, having their heads about 2550, 2592, 2620, 2665, 2700, 2745, 2785, 2830, 2920. These bands were also present, in an ill-developed form, and superposed on continuous spectrum, in the carbon disulphide flame. They appeared also in the spectrum of impure sulphurous anhydride in a vacuum tube, while the less refrangible group previously described was absent.

Further investigations will be undertaken to determine whether the different groups of bands represent different compounds of sulphur, or sulphur in different molecular states.

Compounds of Carbon.

The introduction of many of the compounds of carbon into the nitrogen afterglow results in the development of the spectrum of cyanogen, and direct chemical evidence of the formation of cyanogen has been obtained.† The cyanogen spectrum was strongly developed in cyanogen, ethyl iodide, chloroform, carbon tetrachloride, and acetylene, and it was also seen, with less intensity, in methane, pentane, ethylene, alcohol, ether, and benzol. An investigation of the spectra thus obtained, however, has revealed some interesting peculiarities.

The cyanogen spectrum, as given by the flame of the burning gas, has long been recognised as consisting of two principal sets of bands. One of them occupies the red, yellow, and green parts of the spectrum, and the flutings composing the bands are degraded to the red. The other consists of groups of flutings in the violet and ultra-violet, degraded to the violet, which are especially well known in consequence of their great brilliance in the spectrum of the carbon arc. For convenience of reference, these two sets of bands may be distinguished as the red and violet groups respectively. In addition, there are four groups of fainter flutings in the ultra-violet, degraded to the red, which have been regarded as the probable "tails" of the violet bands.*

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* The chief bands of the CS_2 flame spectrum are about 3370, 3420, 3500, 3557, 3590, 3645, 3680, 3740, 3835, 3940, 4050, 4080, 4160, 4200, 4275, 4310, 4440, 4480.

† R. J. Strutt, *loc. cit.*, p. 228.

The different compounds of carbon do not all behave in the same way when in contact with active nitrogen. In most cases, the "flame" produced was of a lilac tint, very similar to that of the cyanogen flame, but in the case of carbon tetrachloride, or chloroform, the flame was orange in colour and more luminous, and the red spectrum of cyanogen was more strongly developed in relation to the violet.

The "Red" Bands.—In carbon tetrachloride (Plate 6, fig. 3) and chloroform the red spectrum is very brilliant, and is particularly free from contamination with other spectra. The photographs give only feeble indications of the stronger of the second positive bands of nitrogen, and they show no traces of carbonic oxide, or of the Swan bands of carbon. Moreover, the system of bands can be traced clearly into the blue-green and blue, where there are several easily visible bands which are not seen, or only seen with difficulty, in the ordinary flame or vacuum-tube spectrum. This method of producing the spectrum accordingly offers special advantages for the study of the regularity of the bands, and it has been utilised by Messrs. Fowler and Shaw in a separate investigation of the red cyanogen spectrum as obtained from different sources.† Previous accounts of this spectrum have been very incomplete, and only roughly approximate wave-lengths of the bands have been available.

In the small scale photograph reproduced in fig. 3, and in visual observations, the bands appear to follow each other at nearly equal intervals and to show no marked discontinuity as regards their intensities. Other photographs taken with shorter exposures, however, show that the principal bands occur in groups of three, of which the middle one is the brightest in each case. It has been found that all the bands can be arranged in seven regular series, similar to those which constitute the first positive band spectrum of nitrogen.

The Violet Bands.—The familiar cyanogen bands in the violet and ultra-violet are greatly modified in all the carbon compounds which produce a visible luminosity when they are brought in contact with active nitrogen.

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* King, 'Astrophys. Journ.,' 1902, vol. 14, p. 323; Jungbluth, 'Astrophys. Journ.,' 1904, vol. 20, p. 237.

† 'Roy. Soc. Proc.,' this vol., p. 118.

Considerable resolving power is necessary to show the character of the changes clearly, and the Littrow spectrograph was utilised in obtaining the comparative spectra which are reproduced on an enlarged scale in Plate 6, figs. 4 and 5. It will be seen that the details of the violet groups are very different in the glow as compared with the carbon arc.

Taking the 4216 band of the glow spectrum as a typical case, there is a modified development of the structure lines proceeding from the first and third heads (counting from red to violet, or right to left), and a partial suppression of the second and fourth heads. The structure lines emanating from the first head are identical with lines in the corresponding part of the arc band, but there is a conspicuous interruption of the sequence at a short distance from the head, after which the lines became stronger and overrun the second head, which itself appears to be rather weak. A similar effect is observed in the case of the third head, the structure lines of which overrun the fourth, but the third head is not nearly so strong as the first.

These effects are apparently identical with the variations in the negative band of nitrogen 3914, and in the cyanogen band 3883, which have been observed by Deslandres* as the pressure was reduced from one atmosphere to a few millimetres. We have confirmed this observation in the case of the first heads of the cyanogen bands 4216 and 3883, and the differences between the glow and arc bands, to which reference has so far been made, are therefore probably due, either directly or indirectly, to the fact that the cyanogen bands in the glow were produced at a relatively low pressure (5 to 10 mm.).

A still more striking difference between the glow and arc bands occurs in the most refrangible part of each of the violet groups. There is a special increase of intensity in this region, which may possibly be due to a local intensification of some of the series of structure lines, or to the introduction of entirely new bands. Until still greater resolving power can be employed, it will be difficult to determine the exact nature of the difference, but the development of new bands offers the simplest explanation. In favour of this view is the observation that the structure lines of the glow bands do not all occur in the bands of the arc, and also the fact that in some of the photographs (*e.g.* in cyanogen, Plate 6, fig. 6*a*) the supposed new bands are far stronger than the first heads of the groups. Assuming that new bands are developed, their less refrangible edges would be about 4495 (in the 4606 group), 4153 (in the 4216 group), and 3850 (in the 3883 group). Each band must then be supposed to consist of a group of close lines extending over about 9 tenth-metres, this group being followed by a gap of about 3 tenth-metres, and this again by another group of lines extending over about 10 tenth-metres. The "new" bands are especially intense in ethyl iodide, cyanogen, and acetylene; they are also well marked in ethylene and chloroform, but are not nearly so pronounced in carbon tetrachloride.

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* 'Comptes Rendus,' 1904, vol. 139, p. 1179.

Stimulation of cyanogen by the nitrogen afterglow is not the only means of producing these new bands, as they also appear on the photographs of the spectrum produced by the phosphorescent combustion of cyanogen in ozone.*

We have not yet succeeded in obtaining the new bands clearly in vacuum-tube discharges through cyanogen, but there were feeble indications of their presence when wide discharge tubes were employed.

Special care has been taken to show that the spectrum given by cyanogen itself in the nitrogen afterglow has the same peculiarities as that produced from other carbon compounds. When the cyanogen from mercuric cyanide is merely passed through a phosphorus pentoxide drying tube, the removal of water vapour is not complete, and the hydrocarbon band 4315 usually appeared in the spectrum obtained. It seemed possible, therefore, that the modifications of the violet bands in this case might result from the presence of hydrocarbons formed by interaction of water vapour with cyanogen. An experiment was accordingly made in which the cyanogen introduced into the afterglow had been kept in contact with the drying agent for five days. In this case (fig. 6*a*) the hydrocarbon band did not appear, but the violet cyanogen bands presented the same appearances as before. Hence, the stimulation of ready-made cyanogen by active nitrogen produces the same modifications of the violet bands as are observed when the gas is produced by the interaction of nitrogen with other carbon compounds which give luminous effects. The modified bands therefore do not represent cyanogen in course of formation, as might, perhaps, have been supposed. As previously suggested,† it would seem that cyanogen is immediately produced by admixture of the carbon compounds with active nitrogen, and that the observed spectrum is due to the subsequent stimulation of the gas by the peculiar conditions existing in the afterglow.‡

The Cyanogen "Tail" Bands.—The ultra-violet groups of flutings, fading towards the red, which have been regarded as tails of the violet groups, are also very considerably modified in the glow cyanogen as compared with their appearances in the carbon arc (Plate 6, fig. 6, where the bands in the arc are indicated by black dots). So far as can be determined from the photographs available, including some taken with the Littrow spectrograph, the bands are changed in the glow in the same manner as the first heads of the 4216 and 3883 groups; that is, there is an intensification of the structure lines near the head of each band, a conspicuous break in the sequence of the lines at a short distance from the head, and a greater development of the lines immediately following the break. It is probable that a complete investigation of the structure of these bands, in relation to the modified violet bands, would throw additional light on the supposed connection of the two groups, but it would be a laborious piece of work, and cannot at present be undertaken. In addition to the bands noted by King at 3910, 3945, 3985, there is evidently one near 3883, and another about 4030.

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* R. J. Strutt, 'Phys. Soc. Proc.' The "unknown" bands mentioned in this paper as occurring at 431 and 415 appear to be respectively the hydrocarbon band 4315 and the new band of cyanogen 4153. The cyanogen band 4606 is also represented by a band about 450, which would correspond with another of the new cyanogen bands.

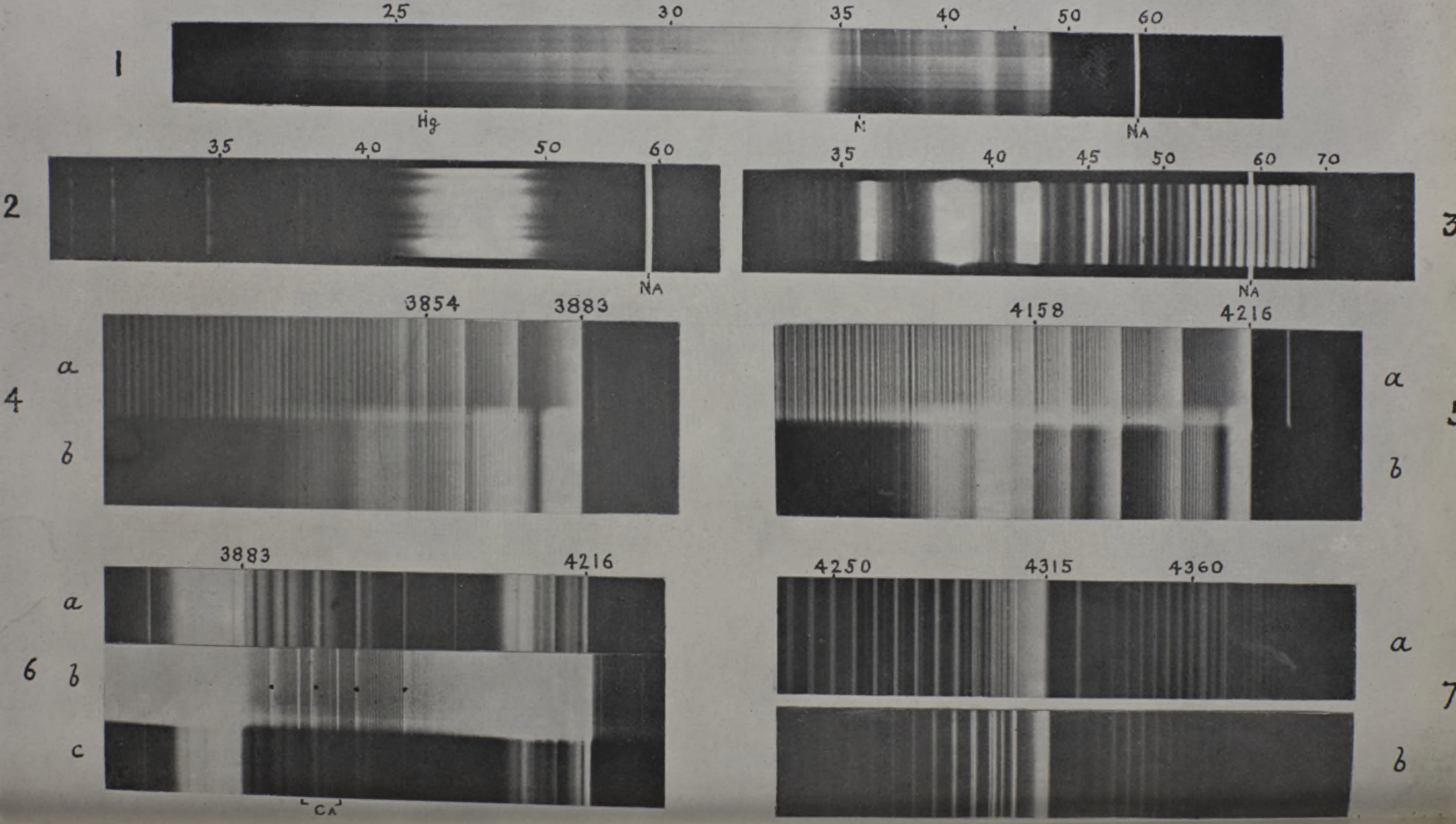
† R. J. Strutt, 'Roy. Soc. Proc.,' vol. 85, p. 228.

‡ It should be mentioned that the photographs of the spectrum generated by the specially dried cyanogen in the afterglow of nitrogen show two of the bands (4679 and 4365) of the "high pressure" spectrum observed in carbon monoxide by Fowler

The Hydrocarbon Band 4315.—The hydrocarbon band 4315 appeared in the glow spectrum in the case of carbon compounds which contain hydrogen, and in cyanogen which had not been completely freed from water vapour. Like the cyanogen bands, this also shows very considerable modifications as compared with the bands obtained from flames. This will be seen from Plate 6, fig. 7, in which the band given by the oxy-coal-gas flame is compared with that given by acetylene in nitrogen. No new lines appear in the glow band, but there are great differences in the relative intensities of the structure lines in the two spectra. Particularly striking is the concentration of luminosity about the head of the band at 4315. This is followed by a dark space about 5 tenth-metres broad, on the more refrangible side, after which there is a special intensification of the first half-dozen structure lines. On the less refrangible side, the flame line 4324 almost disappears in the glow, and the more refrangible members of the group lying between 4335 and 4390 are especially developed. The character of the change corresponds generally with that of the violet cyanogen bands, and of the negative band of nitrogen 3914, under reduced pressure, and the variations are possibly to be accounted for in the same manner.

('Monthly Notices R.A.S.,' vol. 70, p. 490). These bands had not then been observed in any other compound of carbon and were provisionally attributed to carbon monoxide; their presence in cyanogen may have been due to an impurity, or the real origin of the bands may be carbon. The bands in question are generally similar in structure to the new cyanogen bands 4495, etc., and it is remarkable that they occupy positions with respect to the bands of the Swan spectrum corresponding to those which the new cyanogen bands occupy with respect to the violet bands 460, 421, and 388.

SPECTRA DEVELOPED IN NITROGEN AFTERGLOW



Summary and Conclusions.

(1) The spectra generated by the nitrogen afterglow do not differ fundamentally from those which can be produced by other means of excitation. In many cases, however, band spectra are better displayed in the glow, and the more refrangible parts of the spectrum are more completely developed. The method therefore adds to our resources for the production of spectra.

(2) The spectra of metallic substances approximate to those obtained in the electric arc, or are intermediate between arc and flame spectra. In the case of sodium, when sufficiently heated, the maximum intensity in the principal series is at λ 3303, the D lines being nearly extinguished.

(3) The spectra given by iodine, chloride of tin, and mercuric iodide are very similar to those obtained from vacuum tubes. There is, however, a greater development of the more refrangible parts of the spectrum in the case of the glow.

(4) The band spectrum of cuprous chloride is more completely developed in the glow than in the Bunsen flame. It shows an additional series of bands in the ultra-violet which is probably related to the series which constitute the flame spectrum.

(5) The spectra exhibited by sulphur, sulphuretted hydrogen, and carbon disulphide consist of bands which are quite distinct from those given by sulphur in a vacuum tube, but resemble the bands of the carbon disulphide flame in air.

(6) The cyanogen spectrum which is developed in the glow by cyanogen and certain other compounds of carbon differs in several respects from that observed in the cyanogen flame or carbon arc. Some of the differences appear to be due to the production of the spectrum at a relatively low pressure in the glow. A new set of bands, occupying positions near the more refrangible edges of the violet groups, occurs in the glow spectrum, and has also been observed during the phosphorescent combustion of cyanogen in ozone.

DESCRIPTION OF PLATE.

(1) Spectrum of iodine in afterglow.

(2) Spectrum of stannic chloride in afterglow.

(3) Spectrum of cyanogen produced by carbon tetrachloride in afterglow.

(4), (5) The cyanogen bands 4216 and 3883; (*a*) as given by carbon arc in air; (*b*) as given by acetylene in the afterglow.

(6) A group of "tail" bands of cyanogen; (*a*) and (*c*) as given by cyanogen and carbon tetrachloride respectively in the afterglow; (*b*) as given by the carbon arc in air. The marked heads are 3910, 3945, 3985, 4030. The greater development of the new bands 4153, 3850, by cyanogen, as compared with carbon tetrachloride, is also shown.

(7) The hydrocarbon band 4315; (*a*) as given by the oxy-coal-gas flame; (*b*) as given by acetylene in the afterglow.

The Less Refrangible Spectrum of Cyanogen, and its Occurrence in the Carbon Arc.

By A. Fowler, A.R.C.S., F.R.S., Assistant Professor of Physics, and H. Shaw, A.R.C.S., F.R.A.S., Demonstrator of Astrophysics, Imperial College of Science and Technology, South Kensington.

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[Plate 7.]

Introductory.

In connection with Prof. Strutt's investigations of the interaction between the active modification of nitrogen and certain compounds of carbon,* it became necessary to compare the resulting spectra with the spectrum given by cyanogen under the more usual conditions of experiment. It was then discovered that while precise measurements of the well known bands in the violet and ultra-violet had been made by Kayser and Runge, only roughly approximate positions had been tabulated for the bands, degraded in the opposite direction, which appear in the less refrangible parts of the spectrum. In view of the interest of these bands, arising from their possible occurrence in association with the violet bands in certain celestial bodies, as well as from the regularity of their structure, a new series of measurements has been undertaken.

The spectrograph chiefly employed for the determination of positions was one of the Littrow type, giving a linear dispersion of 57 tenth-metres per millimetre at 6700, and 16·5 tenth-metres per millimetre at 4700, the length of spectrum between these points being 6·7 cm. A quartz spectrograph giving 2 cm. for the same range of spectrum was also utilised for ready comparison of the spectra obtained from different sources.

Sources of the Spectrum.

The spectrum has been obtained from different sources, as follows:—

Flame.—The cyanogen was prepared by heating mercuric cyanide, and after drying by passage through a tube containing phosphorus pentoxide it was burned at a glass nozzle. In some of the observations the flame was surrounded by a glass chimney into which a stream of oxygen was passed, and under these conditions the intensity of the spectrum was greatly increased.

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* 'Roy. Soc. Proc.,' 1911, A, vol. 85, p. 228.

Vacuum Tube.—On account of the rapid decomposition of the gas by the electric discharge, a constant stream was passed through the vacuum tube during the exposure of the plates, which amounted in some cases to more than three hours. An "end-on" tube was of necessity employed, because of the dark deposit of paracyanogen which is quickly formed on the walls of the tube in the path of the discharge. It was further necessary to remove and clean the glass or quartz plate through which the light was transmitted to the spectrograph, about once in 20 minutes.

As obtained in this way the bands were very brilliant, and with careful adjustment of the supply of gas the spectrum was more easily maintained than in the case of the flame.

Active Nitrogen.—Prof. Strutt has shown that when certain compounds of carbon such as acetylene and carbon tetrachloride are brought in contact with "active nitrogen," the resulting luminous glow or flame gives a brilliant spectrum of cyanogen. In the case of acetylene, the flame is of a lilac tint, like that of the burning gas, but with carbon tetrachloride the luminosity is orange in colour and the red spectrum of cyanogen is more strongly developed in relation to the violet. The cyanogen spectrum produced in this way from carbon tetrachloride offers special advantages for investigations of the regularity of the bands, in consequence of the better development of the more refrangible bands of the series, which are very feeble in the spectra obtained from the other sources. The violet cyanogen bands in this spectrum are considerably different in detail as compared with those given by the cyanogen flame or carbon arc.* For convenience of reference the cyanogen spectrum obtained by the aid of active nitrogen may be called the "glow-cyanogen" spectrum.

Description of the Spectrum.

The main features of the red cyanogen spectrum, as seen with instruments of small dispersion, are well known. The spectrum consists of a succession of bands—degraded towards the red—which are especially intense in the less refrangible parts of the visible spectrum, and become generally weaker as the blue is approached (Plate 7, figs. 1 and 2). With adequate resolving power each band is seen to be composed of three flutings, the heads of which form a triplet with the narrower pair towards the red. On the more refrangible side of most of the triplets there is an additional faint head, separated from the first component by an interval slightly greater than that between the two closer members of the triplet. The triplets, however, are the most striking features of the spectrum when moderate dispersion is employed.

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* See Strutt and Fowler, 'Roy. Soc. Proc.,' this vol., p. 105.

The spectrum shows considerable variations according to the source from which it is obtained. As will be seen from the data given in Table I, the relative intensities of some of the bands are far from being identical in the different spectra. The band near D (5859) is a notable example, being strong in the vacuum tube and glow-cyanogen spectra, but weak in the flame. Also, the bands more refrangible than 5240 only occur as traces in the flame, but are shown with moderate intensity in the vacuum tube, and better still in the glow-cyanogen. A complete comparison of the spectra from the three sources, however, was complicated by the presence of bands belonging to other spectra in the case of the flame and vacuum tube. In both flame and vacuum tube the bands of the Swan spectrum of carbon appeared, and the hydrocarbon band 4315 was also usually present. The vacuum tube spectrum generally showed, in addition, the carbonic oxide bands 6079, 5610·26, 5198·33, and 4835·44, probably on account of the imperfect removal of water vapour. The vacuum-tube spectrum further differed from the flame spectrum in showing some of the nitrogen flutings, though as a result of the constant changing of the cyanogen in the tube the bands of the first positive group were only shown as feeble traces, and those of the second positive group were not strong enough to be troublesome in the region under investigation.

In accordance with many previous observations,* it was found that when the cyanogen flame was fed with oxygen the whole spectrum was greatly increased in brightness, and that the Swan bands were especially intensified (fig. 4, *a*). The relative intensities of the various cyanogen bands, however, were not greatly affected.

The spectrum produced by carbon tetrachloride in active nitrogen was practically free from contamination with other spectra. There were practically no indications of the hydrocarbon band 4315 or of the bands of the Swan or carbonic oxide spectra. Bands of nitrogen were present, but they were not strong enough to interfere with the identification of the cyanogen triplets.

It should be remarked further that the visibility of the fainter triplets varied greatly with the source and with the dispersion of the instrument employed. In some cases these faint bands were masked by the structure lines emanating from adjacent stronger heads.

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* *E.g.*, Morren, 'Ann. de Chim. et de Phys.,' 1865, series 4, vol. 4, p. 312.

Determination of Wave-Lengths.

The bands in the extreme red were observed visually, and the positions of those less refrangible than 7000 were determined by the use of a wave-length spectroscope.

For the part of the spectrum more refrangible than 7000 the wave-lengths were determined from photographs taken with the Littrow spectrograph, the iron arc being used as a term of comparison. Sufficient iron lines were included in the measures to indicate the corrections to be applied to the wave-lengths calculated by the use of the Cornu-Hartmann formula.

It should be explained that the wave-lengths tabulated can only be regarded as close approximations. As in the case of flutings in general, there is evidence that the heads are complex groups of lines, and the measured wave-lengths will, therefore, depend to some extent upon the dispersion and resolving power of the instrument employed. In order to obtain a consistent system of wave-lengths for discussion of the regularity of the bands, the values tabulated, with the exception of those for the bands in the extreme red, were obtained from a single photograph of the spectrum of "glow-cyanogen," in which the dispersion at D was 38 tenth-metres per millimetre, and the purity of the spectrum at the same place 4000 (fig. 1). Spectra of greater purity were also obtained, but the identification of the heads was in some cases less certain on account of the interference of structure lines belonging to adjacent flutings.

An attempt has been made to include all the fainter bands so as to make the investigation of the structure of the spectrum as complete as possible. Some of the heads would not have been identified as such if their existence had not been indicated by the arrangement of the bands in series.

The positions of the various bands are indicated in Table I. Column 1 gives the wave-lengths, Columns 2, 3, and 4 the relative intensities in the flame, vacuum-tube, and glow-cyanogen spectra respectively, as roughly estimated on a scale of 10 for the brightest band; Column 5 shows the oscillation frequencies *in vacuo*; Column 6 indicates the series to which each band belongs according to the analysis which is given later, and Column 7 the difference (in frequency) between the value observed and that calculated from the series equation.

Table I.

Wave-length.	Intensity.			Oscillation frequency (*in vacuo*).	Series.		O−C.	Remarks.
	Flame.	Vacuum tube.	Glow-cyanogen.		*p.*	*m.*		
7435				13446	76	63	+4	Most refrangible head of a band observed visually.
7283				13727				Visual observations.
7273				13746				
7259				13772	77	64	0	
7119				14043				Visual observations.
7110				14061				
7091				14098	78	65	−4	
6961·6		1	1	14361	74	60	−2	Probable most refrangible head of a faint triplet.
6954·9				14374				
6946·0	2	2	1	14393				
6928·2				14430	79	66	−3	
6818·2				14663				Also a faint head at 6780·2 (14745).
6809·8	<1	2	3	14681				
6793·1				14717	75	61	−2	
6657·2				15017				Also a faint head at 6621·4 (15098).
6648·7	4	9	7	15036				
6632·2				15074	76	62	−1	
6503·0				15373				Also a faint head at 6467·3 (15458).
6494·7	9	10	10	15393				
6479·3				15430	77	63	−1	
6457·0				15483				
6448·9		1	1	15502				
6433·3				15540	73	58	+2	
6355·5				15730				
6347·9	10	9	6	15749				
6332·8				15786	78	64	−1	
6301·8				15864				Also a faint head at 6272·5 (15938).
6294·3		1	2	15883				
6280·0				15919	74	59	0	
6214·4				16087				
6206·7	6	4	1	16107				
6192·3				16145	79	65	+2	
6154·1				16245				Also a faint head at 6124·4 (16324).
6147·4	<1	3	3	16263				
6133·6				16299	75	60	−1	
6013·5				16625				Also a faint head at 5984·9 (16704).
6006·9	2	6	6	16643				
5993·5				16680	76	61	−2	

Table I—*continued*.

Wave-length.	Intensity.			Oscillation frequency (*in vacuo*).	Series.		O−C.	Remarks.
	Flame.	Vacuum tube.	Glow-cyanogen.		*p.*	*m.*		
5866·2		<1	<1	17041	73	57	0	Probable most refrangible head of a faint triplet; other components masked by next band.
5878·3 5872·2 5858·7	2	9	9	17007 17025 17064	77	62	0	Also a faint head at 5850·6 (17078).
5749·3 5743·3 5730·8	5	7	7	17389 17407 17445	78	63	−1	Also a faint head at 5722·4 (17470).
5747·9 5742·2 5729·1		1	1	17393 17410 17450	74	58	−1	Superposed on previous stronger triplet, and not separately observed with small dispersion.
5625·6 5619·4 5607·3		2	2	17771 17791 17828	79	64	0	Overlapped by next band. Both are involved in the 5635 band of the Swan spectrum in the flame and vacuum tube.
5616·3 5611·1 5598·9	3	3	4	17800 17817 17856	75	59	0	Also a faint head at 5591·2 (17880).
5490·8 5485·5 5474·1	2	5	5	18207 18225 18263	76	60	−1	Also a faint head at 5467·4 (18285).
5370·9 5365·6 5354·8	2	4	6	18614 18632 18670	77	61	−2	Also a faint head at 5348·4 (18692).
5255·4 5250·7 5240·2	2	3	5	19023 19040 19078	78	62	−1	Also a faint head at 5233·2 (19104).
5171·6 5167·5 5156·3			1	19331 19346 19388	75	58	+2	Also a faint head at 5150·4 (19411). These are superposed on the 5165 band of the Swan spectrum in the flame and vacuum tube.
5144·9 5139·6 5130·3			1	19431 19451 19487	79	63	0	
5058·2 5054·2 5043·7		1	1	19765 19780 19821	76	59	+1	
4949·7 4945·9 4936·4	1	2	3	20198 20213 20252	77	60	0	Also a faint head at 4931·3 (20273).

Table I—*continued.*

Wave-length.	Intensity.			Oscillation frequency (*in vacuo*).	Series.		O−C.	Remarks.
	Flame.	Vacuum tube.	Glow-cyanogen.		*p.*	*m.*		
4845·9	1	?	4	20630				Also a faint head at 4828·3 (20706).
4842·3				20646				
4833·2				20685	78	61	−1	
4798·1			1	20836				
4794·6				20851				
4785·5				20891	75	57	+1	
4746·0			2	21065				
4742·3				21081				
4733·3				21121	79	62	+1	These are superposed on the 4737 band of the Swan spectrum in flame and vacuum tube.
4694·6			2	21295				
4691·3				21310				
4682·6				21350	76	58	0	

In addition to the bands given in Table I, there were indications of fainter bands, the wave-lengths of which could not be satisfactorily determined from the photographs available. The arrangement of the bands in series, however, permits the calculation of the positions of these faint bands, and for completeness, the calculated wave-lengths of the more refrangible heads are stated below.

Fainter Cyanogen Bands.

Wave-length (air).	Frequency (*in vacuo*).	Series.	
		p.	*m.*
5398·4	18519	73	56
5274·8	18953	74	57
5005·6	19972	73	55
4893·2	20431	74	55
4584·0	21809	77	59
4489·5	22268	78	60
4398·8	22727	79	61
4283·3	23340	77	58

Series Relationships.

The triplets comprising the spectrum appear to be essentially similar to each other, and equally spaced, or nearly so, when estimated on the scale of oscillation frequencies. In the discussion of the distribution of the bands it will therefore suffice to consider the more refrangible members of the triplets.

An analysis of the frequencies has shown that the bands can be arranged in series which are similar to those in which the first positive bands of nitrogen have been arranged by Cuthbertson* and Deslandres.† This is shown in Table II, from which it will be seen that the bands form series of the usual type, whether taken in vertical or horizontal order. The bands in any single series are closely represented by Deslandres' formula, $n = \mathrm{A} + \mathrm{B}m^2$, in which A and B are constants, and m is a number increasing by unity for successive values of n.

If we consider, say, the vertical series, it is clear that the equation calculated from one of them should be applicable to the remainder by a mere change in the value of A, and the figures show that A will vary in such a manner for the different series that it can be represented by another equation of the same form. Hence, all the bands may be included in Deslandres' general equation

$$n = \mathrm{A} + \mathrm{B}m^2 - \mathrm{C}p^2.$$

Table II.—Regularity of Cyanogen Bands (oscillation frequencies *in vacuo*).

79		78		77		76		75		74		73
14430												
1715												
16145	2047	14098										
1683		1688										
17828	2042	15786	2014	13772								
1659		1659		1658								
19487	2042	17445	2015	15430	1984	13446						
1634		1633		1634		1628						
21121	2043	19078	2014	17064	1990	15074						
		1607		1606		1606						
		20685	2015	18670	1990	16680	1963	14717				
				1582		1583		1582				
				20252	1989	18263	1964	16299	1938	14361		
						1558		1557		1558		
						19821	1965	17856	1937	15919		
						1529		1532		1531		
						21350	1962	19388	1938	17450	1910	15540
								1503				
								20891				

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* 'Phil. Mag.,' 1902, [6], vol. 3, p. 348.

† 'Compt. Rend.,' 1902, vol. 134, p. 747.

The coefficients B and C, which are equal to half the second differences in the vertical and horizontal columns respectively, appear to have the same value in the case of cyanogen, and the general equation may therefore be written in the simplified form

$$n = \mathrm{A} - \mathrm{B}(p^2 - m^2).$$

By the use of this equation, a greater range of values of m may be utilised than in calculations based on a single series, and a more accurate representation of the several series may be expected on account of reduced extrapolation. In the actual calculation all the bands have been used in the determination of the constants, and the resulting equation may be written

$$n = 12{\cdot}90\,[(p+0{\cdot}6)^2 - (m+0{\cdot}8)^2] - 9741.$$

For the bands tabulated, p ranges from 73 to 79, and m from 56 to 66, and, as will be seen from the values O—C (observed *minus* computed) given in Table I, the equation represents all the bands very closely, and probably within the limits of error.

Occurrence in the Carbon Arc.

The occurrence of the violet and ultra-violet cyanogen bands (4606·33, 4216·12, 3883·55, 3590·48) in the spectrum of the arc between carbon poles at once suggests that the less refrangible bands under consideration should also appear in company with them. Hitherto, however, their presence does not seem to have been recognised.

Besides the violet and ultra-violet bands of cyanogen, and the Swan bands of carbon (5635·43, 5165·30, 4737·18, 4381·93), the carbon arc shows an immense number of fine lines in the yellow and red, which, so far as we are aware, have not previously been assigned to any definite substance. These lines evidently belong to a banded spectrum, although no distinct heads of flutings are recognisable with the instruments of high dispersion which are most frequently employed for so bright a source (see Plate 7, fig. 5). In observations with small dispersion, however, the lines are seen to be much more densely crowded together in certain places, giving the appearance of ill-defined bands, and comparison photographs, such as those in Plate 7, fig. 4, indicate that these brighter places in the arc spectrum coincide in position with the heads of cyanogen bands. All the chief cyanogen bands from the extreme red to that at 5240 can easily be traced in the arc spectrum in this way.

Conclusive evidence of a close relation between the two spectra is furnished by comparisons obtained with the Littrow spectrograph to which reference has been made. The resolving power of this instrument is sufficient to show a great number of the lines composing the cyanogen bands, while the dispersion is not too great to obscure the corresponding maxima in the spectrum of the arc. The photographs (Plate 7, fig. 2) show very clearly that not only are the brightest places in the arc spectrum coincident with the heads of the cyanogen bands, but that the structure lines are, for the most part, the same in both cases. From the red, as far as the Swan band 5635, the coincidences are very numerous, and some of the separate heads in the cyanogen flutings can be traced in the arc when the cyanogen spectrum is made use of as a guide; the three heads of the band 6333 are especially distinct in the arc spectrum. The comparison clearly indicates that the highly complex spectrum of the carbon arc in the red and yellow is, in the main, due to cyanogen.

The correspondence between the two spectra, however, is not complete when the cyanogen spectrum is obtained from a vacuum tube. While the vacuum-tube spectrum shows comparatively clear spaces between sharply defined bands, the arc spectrum exhibits an unbroken succession of lines with only ill-defined maxima to mark the positions of the heads of the bands. It would thus appear that the condition of the glowing gas in the arc is not identical with that of the gas in the vacuum tube. Other comparisons have shown, however, that a closer resemblance to the arc spectrum is given by the flame of cyanogen, either when the gas is burning in ordinary air or fed with oxygen. In this case the bands are less clearly separated than in the vacuum-tube spectrum, and the heads are less distinctly marked, when the dispersion is sufficient to resolve the bands into their component lines (Plate 7, fig. 3). Further, the arc bands, as a whole, are more like those of the flame spectrum in intensities than those of the vacuum tube, the variation of the band near D being especially noticeable. It is probable that the greater similarity between arc and flame than between arc and vacuum tube is to be attributed to the nearer equality of pressure conditions, as some band spectra are known to vary with pressure.*

Experiments on the changes in the spectrum when the arc is surrounded by different gases have yielded additional interesting evidence as to the cyanogen origin of the less refrangible part of the arc spectrum. The arc was enclosed in a glass globe, provided with arrangements for exhaustion, and for the admission of any desired gas.† When the globe was merely evacuated, hydrogen was liberated as the poles became heated, and the arc was then passing in rather impure hydrogen at a pressure of a few millimetres. Under these conditions, the violet bands of cyanogen were much reduced in intensity, and the many-lined spectrum in the yellow and red practically disappeared (fig. 6, *d*), as would be expected on the supposition that this spectrum is due to cyanogen. Hydrogen was itself represented by H_α, etc., and numerous lines of the secondary spectrum, and the hydrocarbon band 4315, which is not seen in the arc in air, was also present. The Swan band 6188 was also at times well developed in the spectrum, presumably because it was rendered more visible by the removal of the cyanogen band lines, on which it is superposed when the arc is observed in air. It would thus appear that the nearly total removal of nitrogen from the vicinity of the carbon poles results in the disappearance of the great majority of the lines in the yellow and red, and thus supports the view that this part of the spectrum of the carbon arc in air is mainly due to cyanogen.

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* Deslandres, 'Compt. Rend.,' 1904, vol. 139, p. 1174.

† See 'Phil. Trans.,' 1909, A, vol. 209, p. 449.

When the arc was passed in oxygen, either at atmospheric or at reduced pressure, the lines in question again disappeared, or nearly so, and the violet bands of cyanogen were weakened as in the previous experiment (fig. 6, *b*). At the same time, the Swan bands in the green were brightened, the orange band 6188 was easily photographed, and another band of the Swan spectrum less refrangible than H_α was occasionally observed. Both the orange band and the less refrangible one doubtless contribute to the spectrum of the carbon arc in air, but even the group beginning at 6188 can only be traced with difficulty. Bands of carbonic oxide, 5610, 5197, etc., were also occasionally seen when the arc was passed in oxygen, and in some of the observations of the arc *in vacuo*.

A similar experiment with chlorine surrounding the arc also indicated that the band lines under consideration were not produced in the absence of nitrogen.

There is accordingly abundant evidence to show that the great majority of the multitude of lines observed in the less refrangible part of the spectrum of the carbon arc in air are due to cyanogen, while a few of them represent the Swan spectrum of carbon. Bands of carbon and cyanogen thus account completely for the arc spectrum as observed under ordinary conditions.

Comparison with Celestial Spectra.

Among celestial bodies the violet bands of cyanogen have been observed in the spectra of the sun, stars of Secchi's fourth type, and comets. The laboratory experiments have given no evidence that the violet bands can exist apart from the red bands, except to an extent that can be accounted for by the greater intensity of the violet groups. Hence, when the violet bands appear with sufficient intensity in any source, the less refrangible bands may also be expected.

The presence of the ultra-violet band of cyanogen 3883 in the solar spectrum was first shown by Lockyer,* and the tables of Rowland indicate that the bands 4216 and 3590 are also represented among the Fraunhofer lines. All the bands, however, are feeble in the sun, and although the appearance of the less refrangible groups was scarcely to be expected, it nevertheless seemed desirable to make the comparison. Wave-lengths of the necessary degree of accuracy were obtained from photographs of the carbon arc taken with the ten-feet concave grating (fig. 5). Although the heads of the cyanogen flutings cannot be recognised in such photographs, accurate wave-lengths of the lines composing them can be obtained. Portions of the arc spectrum in the neighbourhood of the chief cyanogen bands were measured in detail and compared with the solar lines tabulated by Rowland, but no systematic coincidences could be established. The cyanogen spectrum thus appears to be too feebly developed in the sun to give appreciable indications of the less refrangible system of bands.

A photographic investigation of the Type IV stars made by Hale, Ellerman, and Parkhurst† has demonstrated the presence in the spectra of these stars of the violet bands of cyanogen, in addition to the Swan bands of carbon which were previously identified by Secchi in the visible spectrum. A number of narrow bands in the red and yellow, previously noted by Dunér and Vogel, were also shown in a photograph of the spectrum of 152 Schjellerup, but no significant coincidences with the less refrangible group of cyanogen can be certainly established. As in the solar spectrum. the violet bands do not appear to be sufficiently developed in this star to give much expectation of the visible manifestation of the red and yellow bands. Further comparison should be made when details of the red part of the spectrum become available for those stars of the fourth type in which the violet bands are more strongly developed.

As regards comets, bands in the red have occasionally been noted, but no accurate data are available.

Summary.

1. Revised wave-lengths are given for the bands forming the less refrangible part of the cyanogen spectrum. Numerous bands which have not previously been recorded are included.

2. The heads of the bands can be arranged in regular series similar to those constituting the first positive band spectrum of nitrogen.

3. There are considerable variations in the relative intensities of the

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* 'Roy. Soc. Proc.,' 1878, vol. 27, p. 308.

† 'Pub. Yerkes Observatory,' 1904, vol. 2.

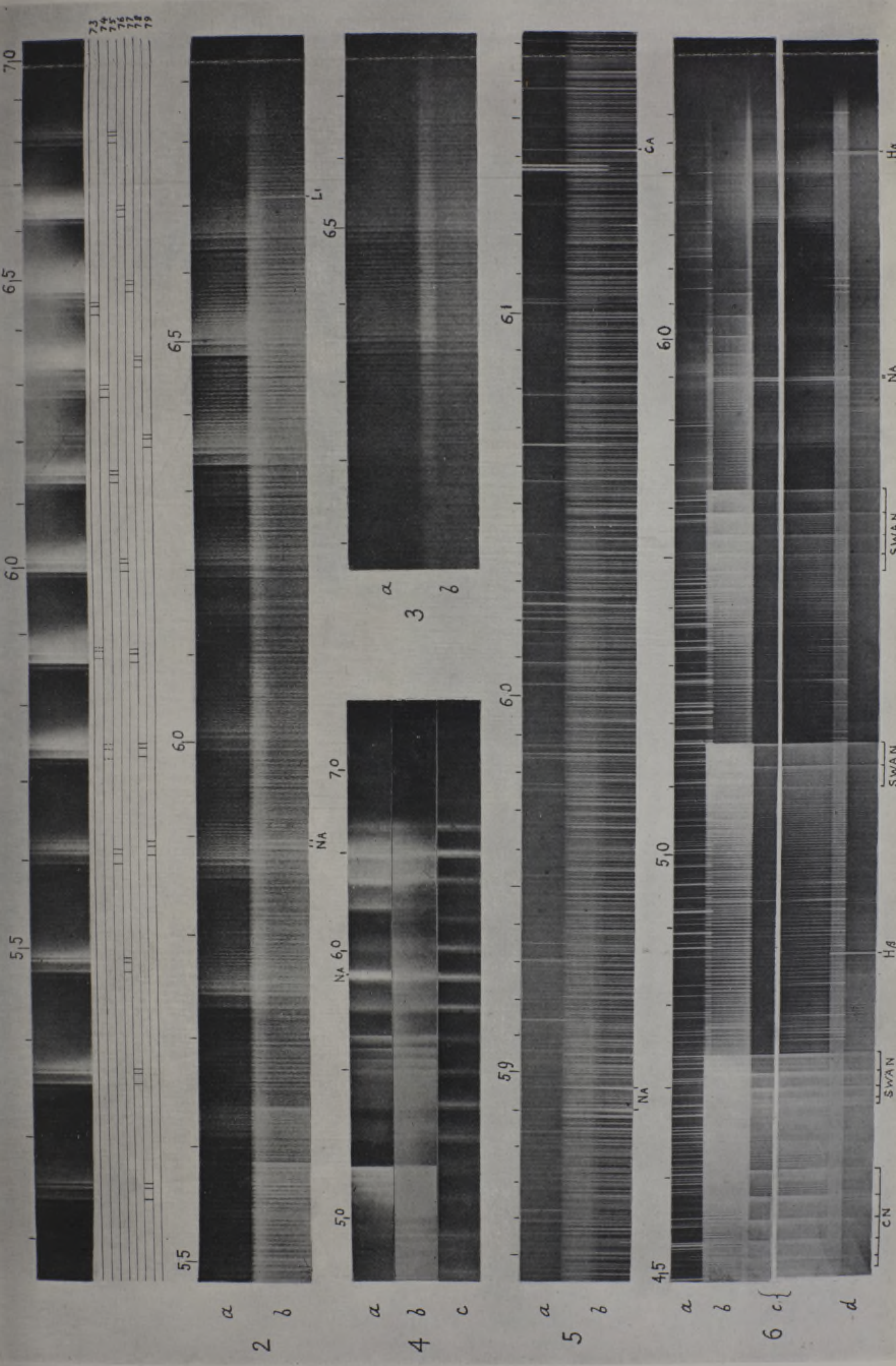
various bands, according as the spectrum is obtained from the flame of the burning gas, from a vacuum tube, or from the luminous glow produced by the interaction of certain compounds of carbon with active nitrogen.

4. The complex spectrum of the carbon arc in the red and yellow is almost entirely due to cyanogen.

5. The spectrum of cyanogen in the sun is not of sufficient intensity to give visible indications of the red and yellow bands. Adequate data for comets and Fourth Type stars are not available for comparison.

DESCRIPTION OF PLATE.

1. Cyanogen spectrum produced by carbon tetrachloride in active nitrogen.
2. (*a*) Vacuum-tube spectrum of cyanogen.
   (*b*) Carbon arc comparison.
3. (*a*) Portion of flame spectrum of cyanogen.
   (*b*) Carbon arc comparison.
4. Small dispersion photographs—
   (*a*) Cyanogen flame fed with oxygen.
   (*b*) Carbon arc.
   (*c*) Cyanogen produced by CCl_4 in active nitrogen.
5. (*a*) Iron comparison spectrum.
   (*b*) Carbon arc (with 10 feet concave grating, 1st order).
6. (*a*) Iron comparison spectrum.
   (*b*) Carbon arc in oxygen at 10 in. pressure.
   (*c*) Carbon arc in air.
   (*d*) Carbon arc *in vacuo* (*i.e.*, hydrogen, etc.).


7,0
6,5
6,0
5,5
73
74
75
76
77
78
79
6,5
6,0
5,5
Li
Na
2
a
b
6,5
3
a
b
7,0
Na 6,0
5,0
4
a
b
c
6,1
6,0
5,9
Ca
Na
5
a
b
6,0
5,0
4,5
Hα
Na
SWAN
SWAN
Hβ
SWAN
CN
6
a
b
c
d

New Series of Lines in the Spark Spectrum of Magnesium.

By A. Fowler, F.R.S., Assistant Professor of Physics, Imperial College of Science and Technology, South Kensington.

(Received June 12,—Read June 26, 1913.)

Introductory.

A recent investigation suggested that the spectrum of hydrogen was unique in having two Principal series of lines which are related to each other in the same manner as Diffuse and Sharp series.* One of these series begins with a line at λ 4686, and the other with a line at λ 3203, the two series converging to the limit 48764 on the frequency scale. The lines in question have so far only been produced by passing powerful discharges through helium tubes (which also contain hydrogen), but in accordance with the work of Rydberg, they have been attributed to hydrogen on the ground of their series relationship with lines known to be due to hydrogen.

In seeking for further examples of such series, analogy with hydrogen suggested spark spectra as the most promising sources. One of the most remarkable spark lines is the well-known line of magnesium λ 4481, which is ordinarily not visible at all in the arc, but is by far the strongest line in the spark. Further, there is a series of single lines in the arc spectrum of magnesium, first identified as such by Rydberg, which it seemed might possibly be analogous to the Balmer series of hydrogen lines. Magnesium therefore appeared to be a very suitable element for investigation, but existing records of the spectrum were altogether inadequate for the purpose in view. There were, in fact, only two recorded lines which could possibly be connected in series with 4481; namely, the lines given by Exner and Haschek at 3106·5 and 2659·5. Other associated ultra-violet lines, however, have now been photographed, and it results that the spark lines form two series like those of hydrogen, 4481 being analogous to the first Principal line of hydrogen 4686.

Method of Observation.

The magnesium spark lines, as ordinarily obtained, are too diffuse for accurate measurement, and it appears from the present investigation that in the far ultra-violet they are even too diffuse to be recognisable. The lines may be narrowed by the use of self-induction, but they are at the same time weakened, and the more refrangible lines were then too feeble for observation. It is known, however, that the spark lines are also brought out when the arc is passed *in vacuo*; that is, in reality, in a low-pressure atmosphere of hydrogen liberated by the heated metal.* Under these conditions the lines are well developed and sharply defined, and by this method it became possible to photograph five additional lines which were evidently related to the three spark lines already mentioned. The apparatus employed was identical with that described in a previous paper for the observation of the spectrum of magnesium hydride.†

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* 'Monthly Notices R.A.S.,' 1912, vol. 73, p. 62.

In addition to the spark lines, the arc *in vacuo* also exhibits the arc and flame lines, and the bands attributed to magnesium hydride. The spark lines, however, are easily identified by comparison with the arc in air. In the region beyond λ 2540, the five new spark lines are, in fact, the only lines present in most of the photographs.‡

An iron arc comparison was utilised in the determination of wave-lengths, except for the extreme ultra-violet, where, in the absence of tabulated iron lines, the comparison spectrum was that of copper.

The New Series of Spark Lines.

Wave-lengths and other details relating to the new series lines are given in the appended tables. The wave-lengths are on Rowland's scale, and the oscillation frequencies have been corrected to vacuum.

A mere inspection of the photographs suggests that the eight lines form a single series having the usual characteristics, but calculations show that they must be divided into two series by taking alternate lines. As the new series consist of enhanced lines, they may be conveniently designated E_1 and E_2, to distinguish them from the other magnesium series, which already include Principal, Diffuse, and Sharp series of triplets in addition to the Rydberg series of single lines.

The Hicks formulæ for the two series, as calculated from the first three lines in each case, are

$$E_1(m) = 49775{\cdot}81 - \frac{109675}{(m + 0{\cdot}996679 + 0{\cdot}001552/m)^2},$$

$$E_2(m) = 49776{\cdot}30 - \frac{109675}{(m + 0{\cdot}496395 + 0{\cdot}002884/m)^2}.$$

Observed *minus* computed values of the frequencies (O – C) are given in Column 6 of the tables.

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* Fowler and Payn, 'Roy. Soc. Proc.,' 1903, vol. 72, p. 253.

† Fowler, 'Phil. Trans.,' 1909, A, vol. 209, p. 449.

‡ See plate accompanying paper by Fowler and Reynolds, this vol., p. 137

Spark Series E_1.

m.	Wave-length (Fowler).	Limit of error.	Oscillation frequency.	Limit of error.	O−C (frequency).	Remarks.
1	4481·35	0·03	22308·5	0·1	0·0*	Strongest line in spark.
2	2661·00	0·05	37569·0	0·7	0·0*	Exner and Haschek's 2659·5.
3	2329·68	0·05	42911·5	0·9	0·0*	Too diffuse for observation in spark.
4	2202·75	0·05	45383·9	1·0	+0·2	" "

* Used in calculation of constants.

Spark Series E_2.

m.	Wave-length (Fowler).	Limit of error.	Oscillation frequency.	Limit of error.	O−C (frequency).	Remarks.
2	3104·91	0·03	32197·9	0·3	0·0*	Exner and Haschek's 3106·5.
3	2449·68	0·05	40809·7	0·8	0·0*	Very diffuse in spark.
4	2253·94	0·05	44353·3	1·0	0·0*	Too diffuse for observation in spark.
5	2166·35	0·10	46146·4	2·0	−0·3	" "

* Used in calculation of constants.

It will be seen that the calculated limits of the two series are practically identical, and that the values of μ differ by very nearly 0·5, as is also the case with hydrogen. The two spark series of magnesium are accordingly similar to the two Principal series attributed to hydrogen, and run nearly parallel to them, as will be evident from the following comparison of the respective frequencies:—

					Limits.
Mg E_1......	22308·5	37569·0	42911·5	45383·9	(49775·8)
H P I ...	21334·4	36574·7	41907·9	44374·2	(48764·0)
Diff.......	974·1	994·3	1003·6	1009·7	1011·8

					Limits.
Mg E_2......	32197·9	40809·7	44353·3	46146·4	(49776·3)
H P II ...	31208·9	39808·2	43348·4	45137·5	(48763·8)
Diff.......	989·0	1001·5	1004·9	1008·9	1012·5

The similarity not only refers to the distribution of the lines in series, but also, to a considerable extent, to the manner in which the two sets of lines are produced.

Besides the above lines, there are four other magnesium spark lines which do not belong to the series. They are very hazy in the spark itself, but are well defined in the arc *in vacuo.* The wave-lengths of these lines are 4384·86, 4390·80, 4428·20, and 4434·20.

Discussion.

If the new magnesium lines are to be regarded as forming Principal series, the Rydberg-Schuster law of limits would lead us to expect associated Diffuse and Sharp series, with their common limit at 49776 − 22309, *i.e.* at 27467. The Rydberg series of single lines, however, has its limit at 26618, and there is apparently no other series which can be supposed to have any closer relation to the spark lines. In the case of hydrogen there is a similar discrepancy, but of much smaller amount; thus, 48764 − 21334 = 27430, while the limit of the Balmer series is actually at 27418·8. It would thus appear that the Rydberg-Schuster law, in its present form, does not accurately connect the spark series with series produced in the arc. Or it may be that the law fails only when there are two Principal series converging to the same limit.

Attention may be called, however, to another possible relation between the spark and the Rydberg series. If, in the application of the Rydberg-Schuster rule, we use the variable part of the E_2 spark equation given by $m = 1$, in place of the actual limit of the series E_1 and E_2, we get a much closer approximation to the limit of the Rydberg series. Thus, $VE_2(1)$* = 48791, and, if the first line of series E_1 be subtracted from this, it gives 26482, differing by 136 from the limit of the Rydberg series. A still closer approximation is obtained if a simple Rydberg equation be calculated for series E_2, namely, from the first two lines,

$$E_2(m) = 49772{\cdot}4 - \frac{109675}{(m + 0{\cdot}498116)^2}.$$

This gives $VE_2(1) = 48867$, and subtracting 22309 as before, the result is 26558, differing by only 60 from the limit of the Rydberg series.

In view of the approximate character of all series equations, there is thus a strong suspicion that the spark series may be related to the Rydberg series in such a way that the limit of the latter is equal to the difference between the variable part of the equation for the second spark series with $m = 1$ and the frequency of the first line of the first spark series. It should be mentioned, however, that, in the case of hydrogen, the discrepancy is slightly increased if this alteration in the Rydberg-Schuster law be made.

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* In this notation V signifies "variable part" of equation.

Until other examples of spark series have been discovered, it is evident that no definite conclusion can be drawn.

An alternative view would be to suppose that the new series, both in magnesium and hydrogen, are series of a new type, having no necessarily simple relation to other series in the respective spectra. In that case the two series attributed to hydrogen might equally be supposed to belong to helium, the presence of which is necessary for their production in the laboratory; it is difficult to believe, however, that the close agreement of one of the series with the Principal series calculated for hydrogen by Rydberg is merely accidental.

Additional Triplets and other Series Lines in the Spectrum of Magnesium.

By A. Fowler, F.R.S., Assistant Professor of Physics, Imperial College of Science and Technology, South Kensington, and W. H. Reynolds, B.Sc., Research Student.

(Received June 12,—Read June 26, 1913.)

[Plate 7.]

Introductory.

Recent photographs of the spectrum of the magnesium arc *in vacuo*, taken primarily for the investigation of enhanced lines,* have revealed several additional members of the triplet and single line series. For some of the previously known lines it has also been possible to obtain improved wave-lengths on account of their greater sharpness under these conditions. It is believed that the results will form a useful contribution to the general study of series lines, and they have accordingly been brought together in the present communication.

For the representation of the series, the Ritz formula, as modified by Mogendorff† and Hicks,‡ has been employed, namely

$$n = n_\infty - \frac{109675}{(m+\mu+\alpha/m)^2},$$

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* See Fowler, this vol., p. 133.

† 'Roy. Acad. Amsterdam Proc.,' 1906, vol. 9, p. 434.

‡ 'Phil. Trans.,' 1910, A, vol. 210, p. 57.

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† 'Roy. Acad. Amsterdam Proc.,' 1906, vol. 9, p. 434.

‡ 'Phil. Trans.,' 1910, A, vol. 210, p. 57.

where n gives the oscillation frequencies of successive lines corresponding to integer values of m; n_∞ is the convergence frequency, or limit, of the series; 109,675 is the general series constant derived from the Balmer series of hydrogen lines; μ and α are constants to be determined for each series. In some cases, it has been necessary to introduce an additional term βm^{-2} in the denominator, as found by Hicks, in order to represent the lines with greater accuracy.

The spectrum of the magnesium arc *in vacuo*, in the visible region, has already been described by Fowler and Payn.* Photographs including the ultra-violet are reproduced in Plate 7. They show the bands attributed to magnesium hydride, together with the lines which are characteristic of the arc, spark, and flame. In the visible spectrum the Rydberg series of single lines is well developed, while in the ultra-violet the triplets and spark lines are striking features. Observations have shown that the spark lines are best developed on the negative pole, while the arc lines are especially conspicuous in the green flame.

In the tables which follow, the wave-lengths are on Rowland's scale throughout, and oscillation frequencies have been reduced to vacuum.

The Diffuse (First Subordinate) Series of Triplets.

Details relating to the Diffuse series of triplets are given in Table I, Kayser and Runge's values being included for comparison so far as they go. The formula calculated for the less refrangible components of the triplets, from the first two and last of the observed members of the series, is

$$D(m) = 39758{\cdot}72 - \frac{109675}{(m + 0{\cdot}831706 - 0{\cdot}007587/m)^2}.$$

The observed *minus* computed values of the frequencies (O − C) are given in Column 8 and it will be seen that this formula does not represent the series quite within the estimated limits of error, but very nearly so. A more accurate representation of the lines is given by including a term βm^{-2}, namely

$$D(m) = 39759{\cdot}06 - \frac{109675}{(m + 0{\cdot}825371 + 0{\cdot}023416/m - 0{\cdot}036786/m^2)^2}.$$

As shown in Column 9 (O − C′), the lines are very closely represented by this equation.

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* 'Roy. Soc. Proc.,' 1903, vol. 72, p. 253.

Table I.—The Diffuse Series of Triplets.

K. and R.		F. and R.						
Wave-length. 2.	Limit of error. 3.	Wave-length. 4.	Limit of error. 5.	Oscillation frequency. 6.	Limit of error. 7.	O−C. 8.	O−C′. 9.	Remarks. 10.
				6798, 6356				Values from the two formulæ.
3838 ·44	0 ·03			26044 ·4 (K. R.)	0 ·2	0 ·0*	0 ·0*	Rowland in Sun 3838 ·44
32 ·46	0 ·03			085 ·1				,, ,, 32 ·45
29 ·51	0 ·03			105 ·2				,, ,, 29 ·50
3097 ·06	0 ·03	3097 ·03	0 ·03	32278 ·8 (K. R.)	0 ·3	0 ·0*	0 ·0*	,, ,, 3097 ·01
93 ·14	0 ·03	93 ·09	0 ·03	319 ·7	0 ·3			,, ,, 93 ·09
91 ·18	0 ·03	91 ·19	0 ·03	340 ·2	0 ·3			,, ,, 91 ·18
		2851 ·76	0 ·03	35056 ·0	0 ·4	−1 ·1	+0 ·3	Separated from strong line 2852 ·22 in 2nd order grating photograph.
2848 ·53	0 ·15	48 ·54	0 ·03	095 ·0	0 ·4			
46 ·91	0 ·15	46 ·88	0 ·03	114 ·9	0 ·4			
2736 ·84	0 ·15	2736 ·63	0 ·03	36530 ·7	0 ·4	−1 ·5	0 ·0*	
33 ·80	0 ·15	33 ·64	0 ·03	570 ·7	0 ·4			
32 ·35	0 ·15	32 ·16	0 ·03	590 ·5	0 ·4			
2672 ·90	0 ·20	2672 ·53	0 ·03	37406 ·8	0 ·4	−1 ·2	−0 ·0	
69 ·84	0 ·20	69 ·66	0 ·03	447 ·0	0 ·4			
68 ·26	0 ·20	68 ·24	0 ·03	467 ·0	0 ·6			
2633 ·13	1 ·00	2632 ·98	0 ·03	37968 ·8	0 ·4	−1 ·3	−0 ·4	
30 ·52	1 ·00	30 ·14	0 ·03	38009 ·8	0 ·4			
		28 ·73	0 ·03	030 ·1	0 ·4			
(2605 ·4)		2606 ·73	0 ·05	38351 ·0	0 ·7	−1 ·3	−0 ·7	
		03 ·98	0 ·05	391 ·5	0 ·7			
		02 ·59	0 ·05	412 ·1	0 ·7			
		2588 ·37	0 ·05	38623 ·0	0 ·7	−0 ·9	−0 ·5	
		85 ·63	0 ·05	664 ·0	0 ·7			
		84 ·32	0 ·05	683 ·6	0 ·7			
		2575 ·02	0 ·05	38823 ·4	0 ·7	−0 ·4	−0 ·1	
		72 ·03	0 ·05	863 ·8	0 ·7			
		70 ·96	0 ·10	884 ·7	1 ·4			
		2565 ·00	0 ·05	38974 ·9	0 ·7	−0 ·3	−0 ·1	
		62 ·30	0 ·05	39016 ·0	0 ·7			
		60 ·96	0 ·10	036 ·5	1 ·4			
		2557 ·29	0 ·05	39092 ·5	0 ·8	−0 ·1	0 ·0	Third member not observed.
		54 ·70	0 ·10	132 ·6	1 ·6			
		2551 ·22	0 ·05	39185 ·4	0 ·8	0 ·0*	0 ·0*	,, ,, ,,
		48 ·56	0 ·10	226 ·2	1 ·6			

* These lines were used in the calculation of constants.

The Sharp (Second Subordinate) Series of Triplets.

Details of the Sharp series of triplets are given in Table II. The formula calculated for the less refrangible components from the first three and the last line is

$$S(m) = 39759{\cdot}18 - \frac{109675}{(m + 1{\cdot}375125 - 0{\cdot}058307/m - 0{\cdot}002355/m^2)^2}.$$

Following Hicks, a term βm^{-2} has been introduced for the better representation of this series, and μ has been taken greater than unity.

It will be seen that the eight lines are represented almost perfectly by the equation given above, and the limit of the series only differs by

Table II.—The Sharp Series of Triplets.

m.	K. and R.		F. and R.		Oscillation frequency.	Limit of error.	O−C (frequency).	Remarks.
	Wave-length.	Limit of error.	Wave-length.	Limit of error.				
1	5183 ·84	0 ·03			19285 ·0	0 ·1	0 ·0*	Rowland in Sun 5183 ·79
	72 ·87	0 ·03			325 ·9			,, ,, 72 ·86
	67 ·55	0 ·03			345 ·8			,, ,, 67 ·50
2	3336 ·83	0 ·03			29959 ·4	0 ·3	0 ·0*	,, ,, 3336 ·82
	32 ·28	0 ·03			30000 ·3			,, ,, 32 ·33
	30 ·08	0 ·03			020 ·1			,, ,, 30 ·04
3	2942 ·21	0 ·3			33977 ·6	0 ·3	0 ·0*	
	38 ·67	0 ·3			34018 ·5			
	36 ·99	0 ·3			038 ·0			A strong line near at 2936 ·61
4			[2781 ·43]		[35942 ·3]		0 ·0†	
			[2778 ·27]		[983 ·2]			
			[2776 ·73]		[36003 ·2]			
5	2698 ·44	0 ·15	2698 ·23	0 ·03	37050 ·5	0 ·4	−0 ·15	
	95 ·53	0 ·15	95 ·28	0 ·03	091 ·1			
	93 ·97	0 ·15	93 ·85	0 ·03	110 ·8			
6	2649 ·30	0 ·50	2649 ·12	0 ·03	37737 ·4	0 ·4	−0 ·1	
	46 ·61	0 ·50	46 ·27	0 ·05	778 ·0	0 ·7		
	45 ·22	0 ·50	44 ·88	0 ·10	797 ·9	1 ·5		
7			2617 ·57	0 ·03	38192 ·4	0 ·4	0 ·0	Third member not observed.
			14 ·74	0 ·05	233 ·6	0 ·7		
8			2596 ·01	0 ·03	38509 ·4	0 ·4	0 ·0*	,, ,, ,,
			93 ·28	0 ·05	550 ·0	0 ·7		

* Used for the calculation of constants.

† The wave-lengths in Column 4 for this triplet were calculated from the formula. The triplet falls in a group of five relatively strong lines, and its components appear to be masked by lines for which the wave-lengths are 2781 ·62, 2778 ·39, 2776 ·86. The other two neighbouring lines are 2783 ·08, 2779 ·94.

0·12 from the limit calculated for the Diffuse series when the term βm^{-2} is introduced.

As regards the agreement of the observed and calculated values, however, an almost equally good result is obtained by taking μ less than unity, so that m is 2 for 5183·84. Using the same lines as before the equation then becomes

$$\mathrm{S}(m) = 39760{\cdot}48 - \frac{109675}{(m + 0{\cdot}361817 + 0{\cdot}039793/m - 0{\cdot}269293/m^2)^2}.$$

The limit is scarcely changed, and the differences O − C are respectively 0·0, 0·0, 0·0, (?), +0·6, +0·5, +0·2, 0·0. Applying Rydberg's law this equation would lead us to expect an ultra-violet series, the limit of which (obtained by putting $m = 1$) would be at 85540, and the first line of the first triplet at 45780 ($\lambda = 2184{\cdot}36$). The observations include the region which would be occupied by this triplet, but the lines have not been observed.

Hence, the first equation is probably correct, as Rydberg's law then indicates a principal series of triplets in the infra-red with its limit at 39759 − 19285 = 20474. This series has apparently been observed by Paschen,* and the limit calculated from the actual lines observed is given by him as 20466·7.

From the data given the mean interval between the first and second members of the triplets in the Diffuse and Sharp series is 40·6, and that between the second and third 20·1. The formulæ connecting the second and third components may accordingly be deduced by subtracting 40·6 and 60·7 from the first terms of the equations representing the first members of the triplets given above.

The Rydberg Series.

As produced in the arc in air, the lines of the Rydberg series of single lines are very diffuse, especially on their less refrangible sides, and except for the first few lines the wave-lengths have not previously been determined with any great degree of accuracy. The arc *in vacuo* gives them quite sharply, and advantage has been taken of this to get better values for the wave-lengths. In Table III the first line is from Paschen; the next three are from Rowland's solar tables; the next four were determined from a photograph of the arc *in vacuo* taken with a 10-foot concave grating, and the last three from photographs with a prismatic spectroscope.

This series has long been recognised as one which cannot be accurately represented by a formula, and the revised wave-lengths provide a further test. The Hicks equation calculated from the first three and last lines of the observed spectrum is

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* 'Ann. der Phys.,' 1909, (4), vol. 29, p. 652.

$$\mathrm{R}_1(m) = 26618{\cdot}20 - \frac{109675}{(m+0{\cdot}314582+0{\cdot}899929/m-0{\cdot}269730/m^2)^2}.$$

The differences, "observed − computed" frequencies, are shown in Column 8.

Table III.—The Rydberg Series of Single Lines.

m.	Previous measures.		F. and R.		Oscillation frequency.	Limit of error.	O − C.	Remarks.
	Wave-length.	Limit of error.	Wave-length.	Limit of error.				
2	8807 ·3 P.				11351 ·1 P.		−186 ·7	P. = Paschen.
3	5528 ·64 R.				18082 ·7 R.		0 ·0*	R. = Rowland.
4	4703 ·18 ,,				21256 ·4 ,,		0 ·0*	K. R. = Kayser and Runge.
5	4352 ·08 ,,				22971 ·1 ,,		0 ·0*	
6	4167 ·81 K. R.	0 ·10	4167 ·55	0 ·02	23988 ·2 F. R.	0 ·1	+0 ·5	F. R. = Fowler and Reynolds.
7	4058 ·45 ,,	1 ·00	4057 ·78	0 ·02	24637 ·1 ,,	0 ·1	+1 ·5	
8	3987 ·08 ,,	1 ·00	3986 ·94	0 ·02	25074 ·8 ,,	0 ·1	+2 ·5	
9			3938 ·58	0 ·03	25382 ·7 ,,	0 ·2	+2 ·8	
10			3904 ·17	0 ·05	25606 ·3 ,,	0 ·3	+1 ·7	
11			3878 ·73	0 ·05	25774 ·3 ,,	0 ·3	+0 ·9	
12			3859 ·39	0 ·10	25903 ·5 ,,	0 ·7	0 ·0*	

* Used in the calculation of constants.

It will be observed that even a four-constant formula does not represent all the observed lines within the limits of error, and that extrapolation to the infra-red member of the series ($m = 2$) is very defective. Further, the negative value obtained by putting $m = 1$ is 2379·7, and this is far from being in agreement with the infra-red line of frequency 5843·6 ($\lambda = 17108{\cdot}1$), which Paschen regards as connected with the Rydberg series. If the infra-red line λ 8807 and the three following lines are used for calculation, the formula becomes

$$\mathrm{R}_1(m) = 26635{\cdot}40 - \frac{109675}{(m+0{\cdot}253055+1{\cdot}247337/m-0{\cdot}790662/m^2)^2},$$

giving O − C, 0·0*, 0·0*, 0·0*, 0·0*, −1·9, −3·6, −5·0, −6·4, −9·2, −11·2, −13·0. The negative value obtained by putting $m = 1$ is now 10883·7, in place of the closer approximation to 5843·6, which might have been expected from the lines employed for calculation.

It is evident that the formulæ given above do not well represent the Rydberg series as a whole. The limit of the series, however, is not likely to be far from the value given by the first formula, namely, 26618·2.

[*Note.*—An interesting result, which follows from the revision of the wave-lengths of the lines of the Rydberg series, is the identification of four additional strong solar lines with lines of magnesium. The details are as follows, including the three lines previously identified by Rowland:—

Table IV.—Rydberg Series in Solar Spectrum.

K. and R.		F. and R.		Rowland.		Intensity in Sun.	Remarks.
Wave-length.	Limit of error.	Wave-length.	Limit of error.	Wave-length in arc.	Wave-length in Sun.		
5528·75	0·10			5528·67	5528·64	8	Previously identified in Sun as Mg.
4703·33	0·05			4703·25	4703·18	10	
4352·18	0·05				4352·08	5	
		4167·55	0·02		4167·44	8	No origin assigned to solar line by Rowland.
		4057·78	0·02		4057·67	7	,, ,, ,,
		3986·94	0·02		3986·90	6	,, ,, ,,
		3938·58	0·03		3938 55	4	,, ,, ,,

It will be seen that the wave-lengths in the sun are consistently lower than the wave-lengths in the arc, but this may perhaps be accounted for by the unsymmetrical character of the arc lines, which are shaded towards the red, and would produce a displacement to the side of longer wave-lengths in the arc measurements. There can be no doubt that the four important solar lines in question should be assigned to magnesium. The remaining lines of the Rydberg series cannot be traced with certainty in the solar spectrum, on account of their superposition on iron lines.]

Other Probable Series of Single Lines.

There are two other magnesium arc lines which appear to be related to the Rydberg series, though no connection has hitherto been recognised. Their wave-lengths, as given by Kayser and Runge, are 5711·56 and 4730·42. Assuming that the two lines are successive members of a series, a simple Rydberg formula gives the limit of the series as 26632·1, which is very nearly that of the Rydberg series. If the limit then be assumed to be identical with that of the Rydberg series (26618·2), a Hicks formula indicates a third line about λ 4354. This line has not previously been recorded, but it is readily seen in photographs of the ordinary magnesium arc taken with adequate exposure and dispersion; its wave-length is 4354·53 ± ·05. The three lines are all of the same character as those of the Rydberg series, but much weaker, and their intensities diminish in passing to the violet in the manner characteristic of series lines. The first line is identified by Rowland with the solar line 5711·31; the second is doubtless identical with the solar line 4730·21, though it is not assigned to magnesium by Rowland; and the third is probably identical with the solar line 4354·43. Adopting the solar wave-lengths as the best approximation to the true wave-lengths of the lines, the Hicks formula is

$$R_2(m) = 26620{\cdot}65 - \frac{109675}{(m+0{\cdot}479157-0{\cdot}032160/m)^2}.$$

Details as to the lines are given in Table V.

Table V.—The Second Series of Single Lines.

m.	K. and R.		F. and R.		Rowland.		Oscillation frequency (Rowland).	Remarks.
	Wave-length.	Limit of error.	Wave-length.	Limit of error.	Wave-length in Sun.	Intensity in Sun.		
2							8542·6	Calculated from formula.
3	5711·56	0·15			5711·31	6	17504·3	
4	4730·42	0·25	4730·34	0·05	4730·21	2	21134·9	
5			4354·53	0·05	4354·43	0 Nd?	22958·8	

The equation for this series suggests that it is of the Sharp or second subordinate type, while the Rydberg series is the associated Diffuse or first subordinate series. If this be so, the variable part of the equation when $m = 1$ might be expected to approximate to the limit of the related Principal series, if such a series exists. The variable part is actually 52380, and the first line of the Principal series would be expected at $52380 - 26620 = 25760$, *i.e.* at λ 3882. There is, however, no appropriate line near this position. In another paper* it is suggested that the Principal series may be the newly recognised spark series beginning at λ 4481 (frequency 22308·5), but this is far from agreeing with the foregoing calculation. It is not impossible that the first member of the Principal series sought for may be the strong arc line λ 2852 (frequency 35056), but the discordance would then be even greater than for the spark series. A formula capable of more general application in the representation of series is greatly to be desired.

For completeness, it should be recalled that there is a feebly developed series of lines which is also associated with the Rydberg series.† The wave-

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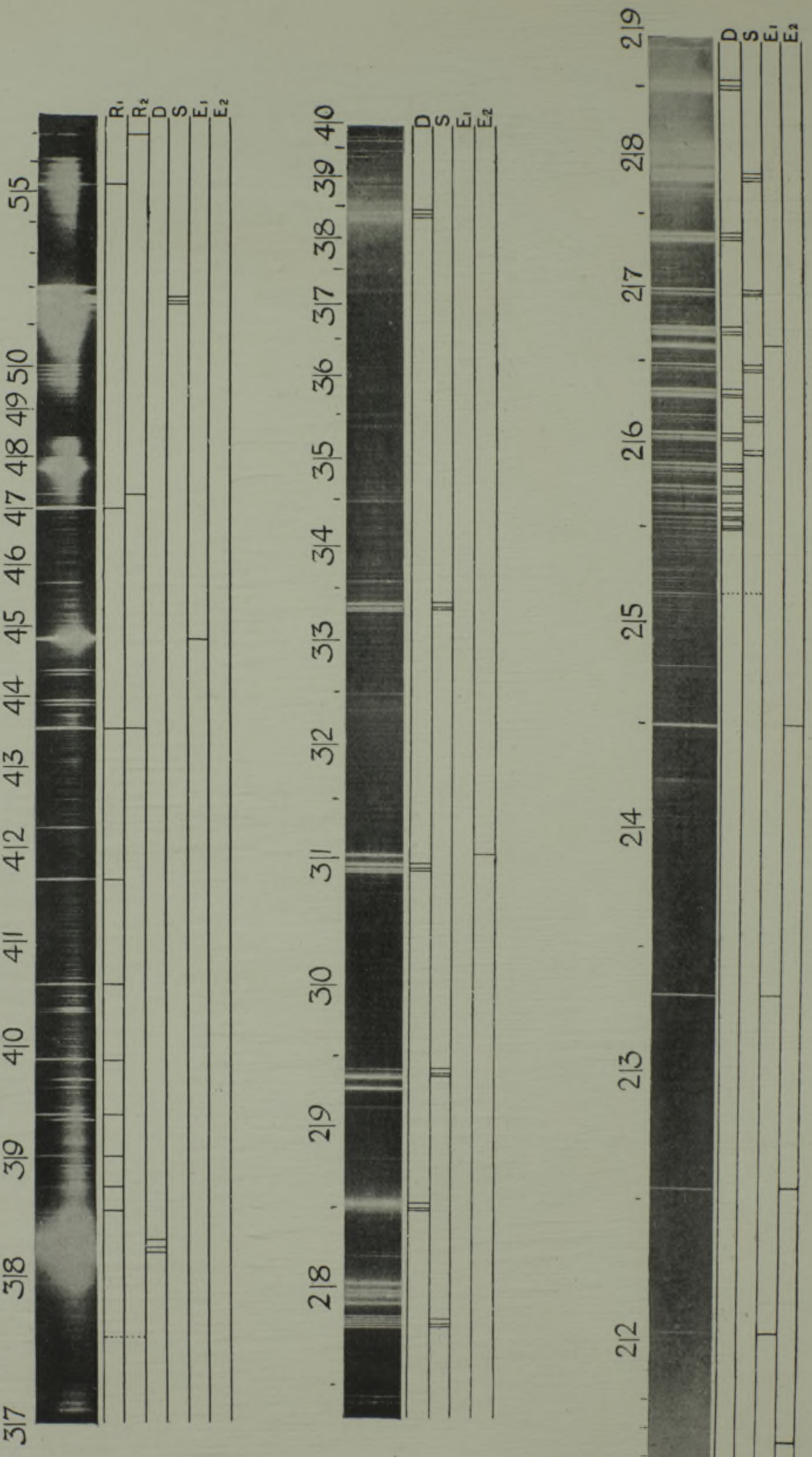
* Fowler, *loc. cit.*

† Fowler, 'Roy. Soc. Proc.,' 1903, vol. 71, p. 420.



Spectrum of Magnesium Arc in vacuo.

lengths of these lines are about 4511·4, 4251·0, 4106·8, 4018·3. A Hicks equation, calculated from the first three lines, gives the limit of the series as 26633·2, while if the term βm^{-2} be introduced by using all four lines the calculated limit is 26613·0. These are as near to the limit of the Rydberg series as can be expected from the approximate wave-lengths which can alone be obtained. The series may be regarded as a third subordinate one.

Summary.

1. Eight additional triplets have been measured in the spectrum of the magnesium arc *in vacuo*, six of which belong to the Diffuse and two to the Sharp series. For some of the previously known lines improved wave-lengths have also been obtained.

2. Four additional members of the Rydberg series of single lines have also been photographed. Even a four-constant formula does not accurately represent this series.

3. Four strong solar lines of previously unknown origin have been identified with lines of the Rydberg series, namely, 4167·44, 4057·67, 3986·90 3938·55.

4. A previously unrecorded line at 4354·53 may be united in a series with the known lines 5711·31 and 4730·21 having the same limit as the Rydberg series. This series is probably of the Sharp or second subordinate type.

DESCRIPTION OF PLATE.

The photographs show the spectrum of the magnesium arc *in vacuo* between wave-lengths 5750 and 2160, and indicate the various series in which the lines have been classified. The letters at the side have the following significance :—

R_1, Rydberg series of single lines.
R_2, Probable second subordinate to Rydberg series.
D, Diffuse (1st sub.) series of triplets.
S, Sharp (2nd sub.) series of triplets.
$\left.\begin{matrix}E_2\\E_1\end{matrix}\right\}$ Series of spark lines.

In addition to lines of magnesium, the photographs show the magnesium hydride bands in the neighbourhood of 560, 521, and 480, and a background of faint lines due to the same substance. There are also a few lines due to impurities of calcium, iron, and manganese, the most prominent being those of calcium at 3934, 3968, and 4227.

BAKERIAN LECTURE: *Series Lines in Spark Spectra.*

By A. Fowler, F.R.S., Assistant Professor of Physics, Imperial College, South Kensington.

(Lecture delivered April 2,—MS. received April 20, 1914.)

(Abstract.)

The classical work of Rydberg, and that of Kayser and Runge, dealt chiefly with series lines occurring in spectra which are produced in the electric arc, or in vacuum tubes with discharges of moderate intensity. In the present communication the lines considered are some of those which are specially developed in the condensed spark; that is, lines which belong to the class of "enhanced lines" as defined by Lockyer.

The investigation was undertaken in connection with the new lines (λ4686, etc.) which were produced in 1912 by passing strong discharges through helium tubes, which always contained an impurity of hydrogen.* These lines are of great interest in celestial spectroscopy, and, following Rydberg, they were at first attributed to hydrogen; they appeared to be closely related to the hydrogen series, while showing no relation to the known series of helium. In addition to the lines calculated by Rydberg for the "Principal" series of hydrogen, however, the "4686" series included an intermediate series which the recognised formulæ suggested was a second "Principal" series, having a simple relation to the first. As the lines could not be obtained from hydrogen alone, it was soon felt that further enquiry should be made as to the value of the numerical evidence on which their assignment to hydrogen was chiefly based. A search for other series of similar character was therefore instituted in the hope that some generalisation with regard to them might be reached.

The conditions of appearance of the lines in helium tubes suggested spark spectra as the most promising source of such series, and a subsequent investigation of magnesium showed that the well-known spark line λ4481 was the first member of a series of the kind looked for. No satisfactory evidence of relation to other series of magnesium was then obtained, and it seemed possible that both the "4686" and the "4481" series might be of a new type, having no necessarily simple relation to other series in the respective spectra.†

The lines of the "4686" series, and the associated "Pickering" series, have

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* 'Monthly Notices Roy. Astro. Soc.,' vol. 73, p. 62 (December, 1912).

† 'Roy. Soc. Proc.,' A, vol. 89, p. 133 (June, 1913).

since become of increased importance, in connection with theories of the constitution of the atom, through the theoretical investigations of Dr. Bohr, who explains them as being produced during the first stage in the re-formation of atoms of helium from which both electrons have been removed by the strong discharges employed. Bohr's formula for this series is identical, in a first approximation, with that for hydrogen, except that the Rydberg constant N (= 109,675 for Rowland's scale) has four times its usual value. The two "Principal" series previously assigned to hydrogen were thus united in a single series of a new type, while the Pickering series was made to include additional lines nearly coincident with the Balmer series of hydrogen. It therefore became important to ascertain if such a modified formula could be adapted to the analogous "4481" series of magnesium, and to other series of spark lines if they could be found.

Further investigation of magnesium was also suggested by Dr. King's discovery that the line 4481 is a very close doublet. Two additional members of this series were resolved, and it at once appeared that the series was not of the ordinary Principal type. The new measurements also showed that the eight observed lines could be united in a single series of the new type suggested by the work of Dr. Bohr. Other series of the same kind were found in Lyman's observations of certain "narrow" doublets in the spectra of calcium, strontium, and barium in the Schumann region.

At this stage a valuable contribution to the investigation was made by the work of E. Lorenser,* who had discussed the Lyman lines, and had shown that they formed series of the Fundamental (or "Bergmann") type, associated with the wider doublets which occur in the spectra of these elements. Lorenser does not appear to have recognised that the lines in question belong to the special class of enhanced lines, but his work proved that these lines form a new class of series, and that similar groups of series occur both in arc and spark spectra. The formula employed by Lorenser was of a modified Rydberg form, but further calculations have shown that the individual series, and the relation between the different series of the same element, are better represented by the Hicks formula with 4N for numerator. One peculiarity of these series is that the first pair of the Diffuse series occurs with a negative sign in the formulæ, whereas it appears in arc series as a positive term.

The wider doublets which occur in the spectrum of magnesium are in several respects analogous to the wider doublets of calcium, strontium, and barium, but the negative term of the Diffuse series is lacking, and a Fundamental series which would fall in line with those of the other three elements is also wanting. The use of the Hicks formula shows that the limit of the "4481" series is related to the first *positive* term of the Diffuse series, but the fact that the doublets occur both in arc and spark, while 4481 requires spark conditions, indicates that the relation is probably indirect.

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* 'Dissertation,' Tübingen, 1913.

The character of the spark series system of magnesium has been elucidated by the discovery of a new group of series of narrow doublets, which occur under exactly the same experimental conditions as 4481. Two of these pairs were observed by Fowler and Payn in 1903, and for convenience of reference the new group of series has been designated the "FP" system. It is shown that the "4481" series is the Fundamental series of this group, its limit being derived from the first negative term of the Diffuse series, as in the case of calcium, strontium, and barium. There is evidence that corresponding series in the "FP" and wide doublet systems run parallel to each other, so that data lacking in one may be obtained from observations of the other. Thus it is found that the separation of the "FP" doublets is equal to the calculated separation of the *second* Principal pair of the wide doublets, which lies in the Schumann region and has not yet been observed. Two well-defined combination series, each consisting of seven lines, have also been recognised in the course of the experiments on magnesium, one derived from terms of the Diffuse and "4481" series, and the other entirely from the "4481" series.

From these investigations it follows that two kinds of series have now to be recognised: (1) series of the "arc" type, having Rydberg's N for the series constant; and (2) series of the "spark" or "enhanced line" type, having a series constant equal to 4N. No numerical relations have yet been traced between the two sets of series occurring in the spectrum of the same element.

Returning to the lines produced in helium tubes, it is now clear that the line 4686 and the other lines associated with it form a single series of the enhanced line (4N) type, and that they can no longer be considered to belong to the same group as the Balmer series of hydrogen, which is of the arc (N) type. The close numerical relations indicated by Rydberg's calculations are therefore not significant, and, in view of the experimental evidence, it must be concluded that the "4686" series is not due to hydrogen but to helium, as first suggested by Dr. Bohr from theoretical considerations. In accordance with the convenient nomenclature of Lockyer, they may be designated "proto-helium" lines. Analogy with the "4481" series of magnesium suggests that the "4686" series is primarily of the Fundamental type, while the three associated series may be considered to be coincident with it.

If the Pickering lines are also due to proto-helium, as seems probable, the series must include additional lines which are almost superposed on the

Balmer series. Experimental and astronomical evidence on this point is incomplete, but there is no evidence against this supposition. The assignment of the Pickering lines to proto-helium is supported by the observations of magnesium, since one of the new combination series is related to the "4481" series in exactly the same way that the extended Pickering series would be related to the "4686" series.

The close relations between the lines of hydrogen (real and hypothetical) and some of those of proto-helium is simply accounted for by Bohr's theory of the origin of these spectra. The formulæ, in which p and m can only take integral values, may be written—

Hydrogen ...... $n = \mathrm{N}\left(\frac{1}{p^2} - \frac{1}{m^2}\right)$. $p = 2$ for Balmer series.

Proto-helium... $n = \mathrm{N}'\left(\frac{1}{p^2} - \frac{1}{m^2}\right)$. $\begin{cases} p = 3 \text{ for "4686" series.} \\ p = 4 \text{ for Pickering series.} \end{cases}$

If N′ were exactly equal to 4N, some of the lines of proto-helium would be coincident with those calculated by Rydberg for the Principal series ($p = 1{\cdot}5$ in the first formula) and for the Sharp series of hydrogen ($p = 2$, $m = m + 0{\cdot}5$ in the first formula). The observed values are $\mathrm{N} = 109{,}675$, $\mathrm{N}' = 438{,}879{\cdot}1 \pm 1{\cdot}0$ (the latter from $\lambda\, 4685{\cdot}98 \pm 0{\cdot}01$), and Bohr has shown that their ratio is in very close agreement with his theoretical expressions for these terms when correction is made for the mass of the electron. The above values of N and N′ give a provisional value for the mass of the hydrogen atom in terms of that of the electron as 1836 ± 12; or 1855 ± 12 when the data are corrected to the International scale of wave-lengths.

The well-known line at 4686 which occurs in the solar chromosphere, and in some of the nebulæ, is undoubtedly the proto-helium line, and there are no indications in these spectra of another line at 4688 which would correspond with the calculated Principal line of hydrogen. Until other evidence is forthcoming, it may be considered that the line spectrum of hydrogen consists only of the Balmer series and parallel series in the infra-red and Schumann regions.

In regard to more complex spectra, since N and 4N are constant, or nearly so, for the two classes of series, Bohr's theory suggests that arc series in general are produced by atoms from which only one electron has been removed by the exciting source, while spark series are produced when two electrons have been removed. It has not yet been shown, however, how a single series of hydrogen or of proto-helium comes to be represented by a group of series in other spectra.

The change in the character of the series in passing from arc to spark spectra suggests the possibility of further change in the same direction, leading to series which would require nine times the ordinary series constant in the formulæ representing them. A preliminary examination of terrestrial and celestial spectra, however, has given no indications of the existence of such series.

The Emission of Electricity from various Substances at High Temperatures.

By G. W. C. Kaye, B.A., D.Sc., and W. F. Higgins, B.Sc.

(Communicated by R. T. Glazebrook, F.R.S. Received May 1,—Read May 21, 1914.)

(From the National Physical Laboratory.)

INTRODUCTORY.

In previous papers* an account was given of experiments in which ionisation currents of great magnitude were obtained from carbon at high temperatures. It was remarked that the largest currents appeared to be associated with the expulsion (at about 2000° C.) of impurities, such as silica, alumina and iron, which are always present in commercial carbon. Such a result is perhaps not surprising in view of Wehnelt's† work on the alkaline earths and their large electronic emissivity when raised to a white heat, as for example in a Wehnelt cathode.

Furthermore, Sir J. J. Thomson‡ showed some years ago that oxides, when raised to a red heat in a crucible, gave out an excess of negative electricity, the most copious streams coming from the oxides of calcium and barium.§ The currents generated were such as were readily indicated by an electroscope.

The present experiments (which were carried out some months ago) were undertaken, in the first instance, to investigate the behaviour of the alkaline

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* Harker and Kaye, 'Roy. Soc. Proc.,' A, vol. 86, p. 379 (1912); A, vol. 88, p. 522, (1913). King ('Astrophys. Jour.,' Nov., 1913, p. 330) has since repeated some of the experiments at Mount Wilson in connection with his work on "tube-arc" spectra.

† Wehnelt, 'Ann. d. Phys.,' vol. 14 (4), p. 425 (1904), and 'Phil. Mag.,' July (1905). See also Jentzsch, 'Ann. d. Phys.,' vol. 28, p. 537 (1909).

‡ J. J. Thomson, 'Camb. Phil. Soc. Proc.,' vol. 14, p. 105 (1906).

§ Prof. Thomson showed further that when various salts were heated, the sign of the resulting electrification was the same as that produced by friction of the dry salt when cold.

A consideration of the following Table will show to what degree of accuracy these two empirical laws hold:—

Table IV.

Gas.	T_c/C.	$10^9 \eta_c^2/A$.
Chlorine	1·28	1·02
Bromine	1·25	1·03
Iodine	1·32	1·01

It will be seen that this group of gases in the periodic Table obey laws similar to those which hold for the inert gases.*

A New Type of Series in the Band Spectrum Associated with Helium.

By A. Fowler, F.R.S., Assistant Professor of Physics, Imperial College, South Kensington.

(Received January 19, 1915.)

Introductory.

A previously unknown band spectrum was noticed in the course of experiments on hydrogen and helium made at the Imperial College in 1912, and was further investigated and described by W. E. Curtis in the year following.† An independent account of this spectrum was also given, almost at the same time, by Dr. E. Goldstein.‡ In each case, some hesitation was felt in attributing the new spectrum solely to helium, in consequence of the persistence of traces of hydrogen in the helium tubes employed.

Mr. Curtis found that the band spectrum was best developed, in the wider parts of the tubes, when a discharge with small capacity and a small air-gap was passed through helium at a pressure rather higher than that which is usual in sealed tubes of the gas. The discharge is then quite brilliant, and by giving long exposures, amounting in some cases to seven or eight hours,

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* 'Phil. Mag.,' January, 1911, p. 45.

† 'Roy. Soc. Proc.,' A, vol. 89, p. 146 (1913).

‡ 'Verh. d. Deutsch. Phys. Gesell.,' vol. 15, p. 402 (1913).

Mr. Curtis obtained an excellent series of photographs of the spectrum with the concave grating of 10 feet radius, some of which were in the second and third orders. Photographs with other instruments were also taken by Mr. Curtis, but he has been unable to continue the investigation in consequence of his temporary enlistment. Under these circumstances it has been thought desirable to make a preliminary analysis of the bands, so that attention might be drawn to any points of special interest without undue delay.

As previously described and illustrated by Curtis and Goldstein, the spectrum includes some conspicuous bands with single heads, others with double heads, and a number of complex regions in which no heads are recognisable at sight. A prominent fluting with a single head, beginning at λ 5733, degrades to the violet, but otherwise all the flutings which have been recognised as such are degraded to the red.

The first result of the investigation was the unexpected discovery that the double-headed bands are not arranged according to the usual law of band spectra, but closely follow the law of line series. The structure of the individual bands, however, is essentially the same as that of bands which are distributed in the more usual way; that is, the distances between successive lines of a series form an approximately arithmetical progression. Mr. Curtis's plates show five bands of the main doublet series, and four additional bands in the ultra-violet which plainly belong to it have since been photographed on a small scale.

A fairly conspicuous doublet in the green, λλ 5133, 5108, was not included in the main series, and it therefore became important to search for additional bands, in order to determine if there were other series which might be related to the first. Only one other doublet, a faint one at 3634, 3625, was at first recognised by inspection, and it remained to be seen if others could be picked out in the more complex regions where bands of different types might be superposed. For this purpose, all the individual lines composing the bands between λ 6500 and λ 3347 were measured, so that the special characteristics of the different types of bands could be ascertained. About 1300 lines in all have been measured, but the final determinations of the wave-lengths, with the necessary corrections for temperature and other sources of error, will occupy a great deal of time, and it is not considered desirable to give so long a list until the wave-lengths have been freed from systematic errors. The provisional wave-lengths, however, are adequate for a first discussion.

As a general statement, it may be remarked that the lines composing the single-headed bands show a smaller second difference than those belonging to the doublets, but in each case the second difference increases in passing from bands in the red to those in the violet part of the spectrum. A great many of the band lines can be arranged in series, but comparatively few additional heads have been traced or suspected. Two doublets which are related to those about 5133 and 3634, however, have been identified, and also a few single-headed bands in addition to those tabulated by Curtis. No regularity in the arrangement of the single bands has yet been recognised, and the present paper is accordingly restricted to the consideration of the doublets.

Structure of the Doublets.

The structure of the strongest double band, at λλ 4648, 4625, is illustrated in fig. 1, where the intensities of the component lines are represented roughly by the lengths of the lines in the diagram. In this case, the more refrangible, and weaker, component of the doublet includes seven strong lines, and the less refrangible component at least eight. In each case the lines converge to the observed heads. The "tail" of the band consists of a large number of lines, of which the brightest form the obvious series which is shown in the diagram; the calculated convergence point of this series lies considerably on the violet side of the two observed heads, and the lines cease to be visible before the convergence point is reached. Series of the latter type are very numerous throughout the spectrum; they appear to accompany all the bands, whether single or double, and the second difference is apparently dependent on that in the band with which it is connected.

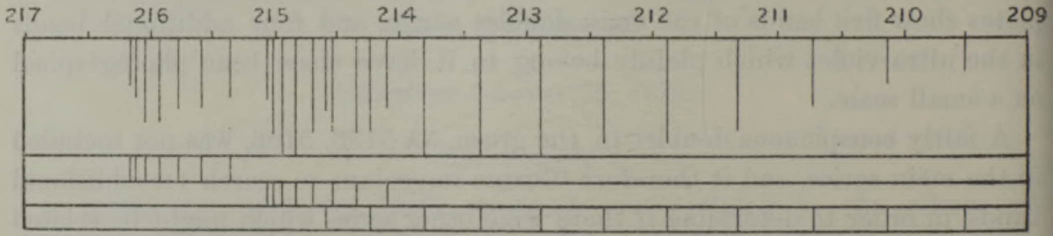

Fig. 1.—The Doublet Band λλ 4648, 4625. (The scale is that of wave-numbers, and only the chief lines are shown.)

The provisional wave-lengths of the lines mapped in fig. 1 are given in Table I, which also shows the corresponding wave-numbers (reduced to vacuum), and the first and second differences. It will be seen that the second differences are approximately constant.

TABLE I.—Details of the Doublet 4625, 4648.

Intensity.	Wave-length (I.A.).	Wave-number.	1st difference.	2nd difference.	Remarks.
4	4625 ·43	21613 ·7	3 ·2		More refrangible head.
5	26 ·12	10 ·5	6 ·7	3 ·5	
7	27 ·54	03 ·8	11 ·3	4 ·6	
7	29 ·98	21592 ·5	15 ·3	4 ·0	
6	33 ·25	77 ·2	18 ·9	3 ·6	
6	37 ·32	58 ·3	23 ·5	4 ·6	
5	42 ·37	34 ·8			
5	4648 ·52	21506 ·3	4 ·0		Less refrangible head.
8	49 ·38	02 ·3	7 ·5	3 ·5	
10	51 ·01	21494 ·8	10 ·9	3 ·4	
10	53 ·37	83 ·9	13 ·7	2 ·8	
8	56 ·35	70 ·2	17 ·1	3 ·4	
8	60 ·06	53 ·1	20 ·4	3 ·3	
8	64 ·48	32 ·7	23 ·4	3 ·0	
6	69 ·58	09 ·3			
6	4658 ·80	21458 ·9	36 ·9		Chief series in tail.
8	66 ·81	22 ·0	40 ·7	3 ·8	
10	75 ·70	21381 ·3	44 ·0	3 ·3	
10	85 ·34	37 ·3	47 ·3	3 ·3	
10	95 ·75	21290 ·0	50 ·1	2 ·8	
9	4706 ·82	39 ·9	53 ·1	3 ·0	
9	18 ·61	21186 ·8	55 ·6	2 ·5	
8	31 ·04	31 ·2	58 ·3	2 ·7	
6	44 ·13	21072 ·9	60 ·1	1 ·8	
4	57 ·69	12 ·8	62 ·4	2 ·3	
3	71 ·86	20950 ·4			

The Main Series of Doublets.

The bands belonging to the main series of doublets are readily recognised on inspection of the photographs. They all occur in regions which are free from complication by the superposition of other bands, and the last seven are apparently the only bands which occur in the ultra-violet between λ 3450 and λ 2950, beyond which the spectrum has not yet been examined. The intensities of the bands decrease gradually in passing along the series.

The wave-lengths (International scale) and wave-numbers (corrected to vacuum) of the heads of these bands are given in Table II; the first three have been derived from grating plates, but the remainder are only approximate values obtained from photographs taken with much smaller dispersion.*

Calculations soon confirmed the suspicion that the series was of the character hitherto exclusively regarded as belonging to line spectra. The series may, in fact, be represented in the usual way by the formulæ of Rydberg or Hicks. For the less refrangible components of the doublets, which are the stronger, the following formulæ have been calculated :—

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* The instruments which would ordinarily have been used for improving on the wave-lengths are detained in Russia, where they were taken for observations of the total solar eclipse of 1914, August 21.

$$n = 34295{\cdot}86 - \frac{109679{\cdot}22}{(m+0{\cdot}928427)^2}, \tag{I}$$

$$n = 34295{\cdot}13 - \frac{109679{\cdot}22}{(m+0{\cdot}931561-0{\cdot}006100/m)^2}. \tag{II}$$

The adopted value of the Rydberg constant is that given by Curtis for the International scale, derived from his measurements of lines of hydrogen.* The differences between the observed and calculated wave-numbers are shown under I and II in Table II, and it will be seen that the bands are represented with quite an ordinary degree of accuracy.

The wave-number intervals between the two components of the doublets diminish in passing to the ultra-violet, but the convergence is less rapid than would be the case if they corresponded with the components of doublets in the Principal series of a line spectrum.

Attempts to unite the more refrangible components of the doublets in formulæ have been less successful. The simple Rydberg formula leaves large residuals, and even the Hicks formula with four constants is not entirely satisfactory. The following formulæ have been calculated :—

$$n = 34330{\cdot}18 - \frac{109679{\cdot}22}{(m+0{\cdot}936830)^2}, \tag{III}$$

$$n = 34324{\cdot}725 - \frac{109679{\cdot}22}{(m+0{\cdot}960333-0{\cdot}045747/m)^2}, \tag{IV}$$

$$n = 34310{\cdot}966 - \frac{109679{\cdot}22}{(m+1{\cdot}051264-0{\cdot}472053/m+0{\cdot}495248/m^2)^2}. \tag{V}$$

The observed *minus* calculated values are shown under III, IV, V in Table II, from which it will be seen that there are considerable systematic residuals in each case. A Ritz formula, with three constants, has also been calculated; it gives residuals slightly larger than those given by formula IV.

In view of the observed rate of contraction of the doublets, the limits given by formulæ III and IV appear to be too high as compared with the limit 34295 for the series of less refrangible heads, which is probably not far from correct. From this point of view, the limit given by formula V would seem to be nearly correct, relatively to that of the less refrangible heads. On the other hand, the position of the band in the infra-red corre-

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* 'Roy. Soc. Proc.,' A, vol. 90, p. 605 (1914).

Table II.—The Main Series of Doublets.

Wave-length (I.A.).	Wave-number.	m.	O – C (Δn).				
			I.	II.	III.	IV.	V.
4648 ·52	21506 ·3	2	0 ·0*	0 ·0*			
4625 ·43	21613 ·7				0 ·0*	0 ·0*	0 ·0*
3676 ·52	27192 ·1	3	+3 ·2	0 ·0*			
3664 ·99	27277 ·6				+24 ·1	0 ·0*	0 ·0*
3356 ·43	29785 ·2	4	+4 ·9	+2 ·6			
3347 ·99	29860 ·3				+30 ·3	+13 ·8	0 ·0*
3206 ·4	31178 ·6	5	+3 ·4	+2 ·1			
3200 ·6	31235 ·1				+16 ·7	+ 7 ·2	−5 ·4
3122 ·7	32014 ·4	6	+3 ·4	+2 ·7			
3118 ·1	32061 ·7				+10 ·8	+ 5 ·9	−2 ·2
3071 ·1	32552 ·9	7	+1 ·9	+1 ·6			
3067 ·4	32591 ·6				+ 2 ·5	+ 0 ·6	−3 ·0
3036 ·8	32920 ·0	8	0 ·0*	0 ·0*			
3033 ·4	32956 ·9				0 ·0*	0 ·0*	0 ·0*
3012 ·5	33185 ·6	9	+2 ·4	+2 ·5			
3010 ·2	33210 ·9				− 8 ·5	− 7 ·1	−4 ·4
2995 ·0	33379 ·0	10	+1 ·5	+1 ·8			
2993 ·0	33401 ·0				−12 ·2	− 9 ·9	−5 ·0

* Used in the calculation of constants.

ponding to $m = 1$ given by V ($n = 8824$) is very discordant with that ndicated for the less refrangible band by I and II ($n = 4803$, 4711, espectively), and a closer agreement in this respect is shown by III and IV $n = 5093$, 4404, respectively).

The difficulty in finding a satisfactory formula for the more refrangible omponents is doubtless associated with the unusual character of the doublet eparations, which resemble neither Principal nor Subordinate series in the ase of line spectra. It may be remarked, however, that some of the known line series are not satisfactorily represented by any of the recognised formulæ.

There is at all events no escape from the conclusion that the doublet bands in question are arranged substantially in the same way as the lines in an ordinary line series.

The Second Series of Doublets.

The first doublet of the second series is quite a conspicuous feature in the green of the visible spectrum, and the third can be recognised without difficulty on the large scale photographs. The heads of the second band, however, occur among other band lines, and were only identified after measurement of the individual lines; the fourth band is very faint, and prolonged exposures would evidently be required to bring out additional members of this series. The positions of these bands are indicated in Table III.

Table III.—The Second Series of Doublets.

Wave-length (I.A.).	Wave-number.	*m*.	O−C (Δ*n*).		
			VI.	VII.	VIII.
5133·34	19475·2	2	0·0*		
5108·22	19570·9			0·0*	0·0*
4002·37	24978·3	3	+0·7		
3989·17	25060·9			+9·4	0·0*
3634·42†	27507·0	4	+1·1		
3624·91	27579·2			+7·1	+2·9
3462·45	28873·1	5	0·0*		
3454·94	28935·9			0·0*	0·0*

* Used in calculation of constants.

† The first line of the head falls on a helium line; its position has been estimated from other lines near the head.

The less refrangible heads of the four observed bands are satisfactorily represented by the following Rydberg formula, as will be seen under VI, Table III:—

$$n = 31956{\cdot}22 - \frac{109679{\cdot}22}{(m+0{\cdot}964402)^2}. \qquad \text{(VI)}$$

The more refrangible heads, as in the case of the main series, are not well represented by a Rydberg formula, and it is probable that even the Hicks formula would be unsatisfactory if a greater number of bands were available to test its applicability. The values of O−C under VII and VIII in Table III refer to the following formulæ:

$$n = 32014{\cdot}42 - \frac{109679{\cdot}22}{(m+0{\cdot}968866)^2}, \qquad \text{(VII)}$$

$$n = 32005{\cdot}665 - \frac{109679{\cdot}22}{(m+0{\cdot}982328-0{\cdot}024835/m)^2}. \qquad \text{(VIII)}$$

Corresponding to $m = 1$, formula VI gives 3534 as the wave-number of the less refrangible component of a possible infra-red member of the series, and formulæ VII and VIII give 3721 and 3382 respectively for the more refrangible head.

Comparison of the Two Series.

It is remarkable that, although the two series of doublets follow the law of line spectra individually, no relation between them corresponding to any which exists between the different members of a system of line series is certainly indicated. The series which has been described as the "main series" of doublets, in consideration of its brightness and extent, would probably correspond with the Principal series in the case of a line spectrum if it had any equivalent. The second series would similarly correspond to one of the subordinate series, and the fact that the first term of the series ($m = 1$) occurs with a positive sign may be taken to indicate that it would be equivalent to a Diffuse series. A third series, which would correspond to the Sharp series in a line spectrum, has not yet been identified. In accordance with well known principles, however, an approximate formula for the Sharp series may be derived from that for the Principal, but neither of two or three additional doublets which have been suspected occupy the positions so calculated.

In a system of line series, as expressed by the Rydberg-Schuster law, the common limit of the Diffuse and Sharp series differs from that of the Principal series by an amount equal to the wave-number of the first Principal line. In the present case the difference between the limits of the two doublet series is about 2340, while the wave-number of the first member of the main series calculated by the formulæ I and II is between 4700 and 4800. The difference appears to be too great to be accounted for by the approximate character of the formulæ employed, and, if so, the two doublet series cannot stand in the relation of Principal and Diffuse series. The same conclusion is suggested by the fact that the less refrangible components of the doublets are strongest in both series.

Thus, although there can be no doubt that the heads of the doublet bands are arranged according to the law of line spectra, other relations shown by the different series of a line system do not appear to hold.

Summary.

The band spectrum associated with helium, as previously described by Curtis and Goldstein, includes bands with single heads and bands with double heads. A preliminary analysis of this spectrum has led to the following conclusions:—

(1) The doublets do not follow the ordinary law of band spectra, but can be arranged in two series of the type hitherto exclusively associated with line spectra, and can be approximately represented by the usual formulæ

involving the Rydberg constant. Nine bands of the main series and four of the fainter second series have been identified.

(2) The two series may be likened to the Principal and Diffuse series in the case of line spectra, but the usual relation between such series is not certainly indicated, and no equivalent of the Sharp series has yet been traced.

(3) The doublet separations are not in accordance with those associated with line spectra; they diminish in passing along the series, but do not vanish at the limit.

No regularity in the arrangement of the single bands has been recognised.

The author is indebted to Mr. F. S. Phillips and to Major-General du Gard Gray, C.B., for photographs of the new band spectrum supplementing those previously obtained by Mr. Curtis.

The Influence of Molecular Constitution and Temperature on Magnetic Susceptibility. Part III.—*On the Molecular Field in Diamagnetic Substances.*

By A. E. Oxley, M.A., M.Sc., Coutts Trotter Student, Trinity College, Cambridge, Mackinnon Student of the Royal Society.

(Communicated by Prof. Sir J. J. Thomson, O.M., F.R.S. Received June 24, 1914.)

(Abstract.)

The work is a continuation of that in 'Phil. Trans.,' A, vol. 214, pp. 109–146, which contains Parts I and II.

The suggestion made at the end of Part II, p. 143, that the local molecular field in diamagnetic crystalline substances may be comparable with the ferromagnetic molecular field, has been justified. Estimates of the order of magnitude of this field have been obtained from the following sources:—

(a) *The change of specific susceptibility accompanying crystallisation.* The extent of this change may be interpreted, on Langevin's theory of diamagnetism, as produced by a local molecular field of the order of intensity 10^7 gauss, which comes into operation on crystallisation (§ 4). This intense local field distorts the molecules and alters the periods of vibration of the contained electrons. From the nature of the structure which has been postulated for a diamagnetic molecule, this field is of an alternating character, the distance over which it is unidirectional being comparable with the

and that when m is even, $|\phi_m|^2 = 0$. The second plate neutralises the reflection from the first plate, the fourth plate that from the third, and so on. The simplest case under this head is when $\delta = \frac{1}{2}\lambda$, $\delta' = \lambda$.

A variation of the latter supposition leads to a verification of the general formulæ worth a moment's notice. We assume, as above, $\delta' = s'\lambda$, but leave δ open. Since $e^{\frac{1}{2}ik\delta'} = \pm 1$, (9) and (10) become

$$r = \mp \frac{e^{\frac{1}{2}ik\delta} - e^{-\frac{1}{2}ik\delta}}{\eta^{-1}e^{\frac{1}{2}ik\delta} - \eta e^{-\frac{1}{2}ik\delta}}, \qquad t = \pm \frac{\eta^{-1} - \eta}{\eta^{-1}e^{\frac{1}{2}ik\delta} - \eta e^{-\frac{1}{2}ik\delta}}; \tag{68}$$

and these are of the form (39), if we suppose $a = \eta^{-1}$, $b = e^{\frac{1}{2}ik\delta}$. The reflection ϕ_m from m plates is derived from r by merely writing b^m for b, that is, $e^{\frac{1}{2}imk\delta}$ for $e^{\frac{1}{2}ik\delta}$, leaving $|\phi_m|$ equal to $|r|$, as should evidently be the case, at least, when $\delta' = 0$.

Absorption Bands of Atmospheric Ozone in the Spectra of Sun and Stars.

By A. Fowler, F.R.S., Professor of Astrophysics, and the Hon. R. J. Strutt, F.R.S., Professor of Physics, Imperial College, South Kensington.

(Received June 13, 1917.)

[Plate 3.]

Introductory.

In a paper communicated to the Royal Society in 1890, Sir William Huggins gave an account of his discovery of a new group of lines in the photographic spectrum of Sirius, situated near the limit of atmospheric transmission.* A photograph taken with a long exposure was described as showing no strong lines after the termination of the hydrogen series until about λ 3338 was reached, at which place there appeared the first of a group of at least six lines, all of which were nearly as broad as those of hydrogen. The third line of the group, about λ 3278, appeared to be the broadest. The sixth line occurred almost at the limit of the photograph, where the spectrum was very faint, and it was not possible to determine whether this was the last member of the group. The wave-lengths of the lines, which were only considered to be roughly approximate, were given as 3338, 3311, 3278, 3254, 3226, and 3199.

In 1915, a copy of an excellent photograph of the spectrum of Sirius,

* 'Roy. Soc. Proc.,' vol. 48, p. 216 (1890).

which had been taken with a small quartz prismatic camera at the Royal Observatory, Edinburgh, was kindly forwarded to us by Prof. Sampson. In this photograph the Huggins group is well shown (Plate 3, fig. 3), and it was at once suspected, from the general appearance of the spectrum, that a system of bands, and not a group of lines, was in question. From our knowledge of the physical conditions in the atmosphere of Sirius, as indicated by other parts of the spectrum, the existence of bands in this star seemed highly improbable, and it was an obvious inference that they might be produced by absorption in our terrestrial atmosphere. This view was strongly supported by photographs of the solar spectrum which we obtained with a small quartz spectrograph near sunset, as compared with similar photographs taken when the sun was at a considerable elevation. The spectrum of the low sun showed very decided indications of bands occupying about the same positions as those in the spectrum of Sirius, but, on account of the superposition of solar lines, the wave-lengths of the bands could not be very certainly derived.

The published results of experiments on the absorption of atmospheric gases suggested that ozone was the most probable source of the bands under consideration. Ladenburg and Lehmann* had, in fact, noted a number of bands in the absorption spectrum of ozone, extending from λ 3220 to λ 3566, and thus covering a part of the region occupied by the bands observed in Sirius. The wave-lengths given by Ladenburg and Lehmann, however, were not in sufficient agreement with those given by Huggins, or with the provisional wave-lengths communicated to us by Prof. Sampson, to establish the identity of the ozone and Sirian bands. As no other probable origin occurred to us, it was decided to make a new experimental investigation of ozone absorption, and, after some unavoidable delay, the experiments were recently undertaken. The new observations have definitely established that ozone is the origin of the Huggins group of bands in the spectrum of Sirius, and that the same bands are also present in the solar spectrum, with an intensity varying with the sun's altitude.

While this investigation was in progress, our attention was drawn by Prof. Sampson to a dissertation by Otto Kohl,† in which the author gives results of measurements of a number of photographs of ultra-violet stellar spectra which had been taken at Potsdam by Prof. Hartmann in 1904. In this paper, the discovery of the bands near the end of the spectrum was wrongly attributed to Prof. Hartmann, but the additional fact was brought out that they occurred in different stars, irrespective of spectral types. Thus, the bands were noted in α Aurigæ, α Canis Majoris, α Lyræ, β Orionis, and ζ Tauri, as well as in the solar spectrum. There were considerable divergences in the measured positions of the bands, but, in view of their diffuseness and their varying breadths in different spectra, it could reasonably be concluded that they were common to the different stars. The occurrence of the bands in different stars naturally suggested that the whole group had the same origin, and that they might possibly be due to absorption by the earth's atmosphere. There was no evidence, however, for attributing them either to atmospheric oxygen, nitrogen, water-vapour, or carbon dioxide, and there appeared to be no agreement whatever between the stellar bands and the bands of ozone, as recorded by Ladenburg and Lehmann. The alternative supposition that the bands might be of stellar origin likewise received no support from comparisons with metallic spectra, and it was concluded that chemical identification would be necessary to decide whether they were of sidereal or telluric origin.

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* 'Ber. Deutsch. Phys. Gesell.,' vol. 8, p. 125 (1906).

† 'Ast. Mitt. König. Sternwarte zu Göttingen,' No. XVI (1913).

It should be mentioned that the bands also appear very distinctly in photographs of the spectra of Capella, Vega, and Regulus, taken at Edinburgh on April 12, 1915, and recently forwarded to us by Prof. Sampson.

Previous Observations of Ozone Absorption.

The general features of the absorption spectrum of ozone have long been known. In the visible spectrum there are several ill-defined bands, which were first described by Chappuis* in 1880. These bands were also obtained, but less strongly, by Liveing and Dewar† in 1889; and, more recently, their positions have been re-determined by Ladenburg and Lehmann.‡ The strongest of these bands, according to Chappuis, extends from λ 6095 to λ 5935.

A region of strong absorption in the ultra-violet was discovered by Hartley§ in 1880. The central part, where the absorption was most intense, was estimated to be at λ 2560, and the band was observed to extend in both directions as the amount of absorbing gas was increased. Hartley concluded, however, that the band would not extend indefinitely with increase in the amount of ozone, and that nearly the maximum effect was produced when all rays with a wave-length less than 2930 were absorbed; that is, it was thought that further additions of ozone would only slightly increase the absorption.

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* 'Comptes Rendus,' vol. 91, p. 985, and vol. 94, p. 858.

† 'Roy. Soc. Proc.,' vol. 46, p. 222 (1889).

‡ *Loc. cit.*, p. 129.

§ 'Jour. Chem. Soc.,' vol. 39, pp. 57 and 111.

Quantitative investigations of the broad ultra-violet absorption band have been made by Fabry and Buisson,* who used a mercury arc as the source of light, and determined the coefficient of absorption for 10 different wave-lengths between 2352 and 3341. The wave-length of maximum absorption was placed at λ 2550, in close agreement with Hartley, and ozone was stated to be as opaque for light of this wave-length as are the metals, mass for mass, for visible light.

The ultra-violet bands which form the chief subject of the present communication occur near the less refrangible boundary of the great absorption band. The only previous observations of bands in this region appear to be those of Ladenburg and Lehmann, to which reference has already been made. Burning magnesium was used as the source of light, and it was stated that with small concentration of ozone there was merely a continuous absorption extending to about λ 3160, while with a large amount of the gas a number of relatively narrow bands were observed near the limit of absorption towards the red. It was further observed that bands appeared at successively longer wave-lengths as the concentration of ozone was increased. With the greatest concentration obtained by Ladenburg and Lehmann, the complete absorption reached as far as λ 3388.

The bands in question probably escaped the notice of Hartley, because the electric spark which he employed as the source of light in his experiments was not well adapted to show them. Fabry and Buisson make no reference to the bands, and it is probable that they also did not observe them on account of the unsuitability of their source of light.

For the sake of completeness, it should be added that the absorption of ozone in the infra-red has been investigated by K. Ångström,† who observed bands which were also found in the solar spectrum.

Experimental Procedure.

For laboratory observations of the absorption bands a source of light is required which yields a spectrum as continuous as may be, and extending far into the ultra-violet. The absorption bands to be looked for, as will appear later, are very faint over a part of their range, and emission lines or bands, due to the source of light used, add greatly to the difficulty of observing them. After trial of various sources, those selected for use were: (1) the incandescent crater of the carbon arc; and (2) the light of burning magnesium ribbon, fed by a clockwork lamp. The carbon arc does fairly well to about λ 3000, but beyond this the continuous spectrum thins out, and lines due to impurities have a disturbing effect. Burning magnesium is less convenient for long exposures, but its continuous spectrum has been photographed as far as λ 2200, and it shows no lines or bands between that and λ 3600, except the strong reversed line at λ 2852.

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* 'Jour. de Phys.,' vol. 3, p. 196 (1913).

† 'Arkiv för Matematik' (Stockholm), vol. 1, pp. 347 and 395 (1904).

The ozone used was prepared in the ordinary way by means of a Siemens ozoniser. Oxygen from a cylinder was bubbled through sulphuric acid, which gave a rough idea of the rate of flow; then it passed through the ozoniser to the observation vessel, through which a continuous flow was maintained.

The observation vessels were of various kinds. For great thicknesses, glass tubes were used, closed by quartz plates cemented on with sodium silicate. The length of these tubes varied from 8 feet to 18 inches. For small thicknesses, the ozone stream was delivered by displacement into silica flasks or test-tubes placed in front of the slit of the spectroscope.

No strict control was kept over the quantities of ozone in use, but the rate of passage and other conditions in the generator were kept fairly constant, so that the length of the vessel afforded a convenient means of varying the amount of ozone producing absorption.

In other experiments, when the long tube was in use, the tube was first filled with ozone, the ozoniser was then put out of action while the gas stream was left on, so that ozone was slowly displaced by oxygen. During this process, a succession of exposures were made, allowing the spectroscopic changes to be traced.

The greatest concentration of the ozone used was probably less than 1 per cent. Ladenburg and Lehmann were not able to trace any bands when using dilute ozone. They had recourse to the troublesome process of concentrating it by liquefaction. We have not found this to be necessary.

The instrument chiefly employed for the photography of the spectra was a small quartz spectrograph by Hilger, giving a linear dispersion of 58 Å. per millimetre at λ 3200. This small dispersion was well adapted for the purpose in view, as most of the bands are rather diffuse, and very precise determinations of their positions are not to be expected. Some of the photographs were taken with copper arc comparisons, and the wave-lengths of the ozone bands were determined in the usual manner by the Cornu-Hartmann interpolation formula.

Photographs of the bands were also taken with a much more powerful instrument, giving a dispersion of 7 Å. per millimetre at λ 3200, but the bands were so diffuse under these conditions that there was no gain in accuracy as compared with the smaller spectrograph. The latter has also the advantage of giving spectra comparable in purity and dispersion with those of the instruments employed for the stellar spectra.

The bands were lost altogether when it was attempted to photograph them in the 3rd order of a 10-feet concave grating.

The New Observations.

The bands in the visible spectrum have not been considered in this investigation, but as regards the ultra-violet region the new observations are in general agreement with those of previous investigators. Additional features, however, have been noted.

The great absorption band in the ultra-violet is illustrated in fig. 1, Plate 3. These photographs were taken with a cadmium spark as the source of light, and show the broadening of the band which accompanies an increase in the amount of absorbing gas.

In opposition to the statement of Ladenburg and Lehmann, the system of narrow bands was found to be represented even with minute amounts of ozone. They were, in fact, photographed as far as λ 2700 when the layer of dilute ozone was only 1 cm. thick. As the thickness of gas was increased, the more refrangible members of the group were obliterated by the increased extent of the great band, and new members continued to appear just beyond the boundary towards the red. There was, however, a general increase in the distinctness of the bands when the region about λ 3100 to λ 3300 was reached. The least refrangible band observed was a very faint one at λ 3432. It would seem that Ladenburg and Lehmann only measured the spectrum with very large concentration, as they recorded no band more refrangible than λ 3220, and their last band towards the red was about λ 3566. The present investigation suggests that the narrow bands continue throughout the whole range of the great absorption band, though they become rather inconspicuous even at λ 2700. The successive appearances of the spectrum with increasing thicknesses of ozone are illustrated in fig. 2, Plate 3. Referring to these spectra, the actual bands seen in (*a*) do not appear in (*b*) or (*c*) because, on account of the general absorption, no light in the region of λ 2800 can get through. And again, the actual bands seen in (*c*) do not appear in (*a*) or (*b*), because there is not enough ozone to bring them out.

As it was not found possible to obtain the desired range of bands in a single experiment, photographs taken with different concentrations of ozone were used for purposes of measurement, and the results combined. The wave-lengths and intensities of all the bands on the red side of λ 3080 which were sufficiently distinct for measurement are included in Table I. The strongest bands are assigned intensity 10, and the faintest intensity 1.

Bands which appear as pairs or groups are indicated as such by connecting brackets, and those which are of more than average breadth are indicated by the letter "*b*" following the intensity number.

Table I.—Wave-lengths of Ozone Absorption Bands.

λ.	Intensity.	λ.	Intensity.
3432·2	1	3232·8	1
3421·4	1	3227·2	10
3402·6	1	3221·5	10
3377·7	1	3206·8	2
3374·1	3	3201·0	8*b*
3365·2	1	3194·8	6
3346·0	1	3188·8	1
3338·5	4	3181·5	1
3331·2	1	3177·0	8*b*
3311·5	5*b*	3171·6	4
3304·1	3	3162·6	2*b*
3284·0	2	3156·1	8
3279·8	8*b*	3137·4	10*b*
3272·0	3	3114·3	8*b*
3255·5	5	3105·0	5
3249·7	8	3096·5	4
3243·0	1*d*	3089·5	8*b*

The wave-lengths of the 12 bands given by Ladenburg and Lehmann, without further description, are 3566, 3503, 346, 3435, 3409, 3376, 3343, 333, 3295, 327, 3235, and 322. The first three are out of range of our observations, and the remainder are not in good agreement with our measures. The band 3295 does not appear in our list, and that at 3235 is only represented by a very faint band at 3232·8. Moreover, the wave-lengths 327 and 322 represent very imperfectly the corresponding groups in our photographs. The strong pairs 3311·5, 3304·1 and 3255·5, 3249·7, which are included in Table I, do not appear at all in Ladenburg and Lehmann's list.

It should be noted that the photographs taken with high dispersion gave no indications of the resolution of the bands into close component lines. A similar result was obtained by Chappuis in the case of the bands which occur in the visible spectrum.

Ozone Bands in the Spectrum of Sirius.

The Edinburgh photograph of the spectrum of Sirius, of which an enlarged copy is reproduced in fig. 3, Plate 3, is on a scale nearly identical with that employed in the laboratory experiments, the dispersion being 56·5 Å. per millimetre at λ 3200. In accordance with the description given by Huggins, there are no strong lines between the end of the hydrogen series and the beginning of the group of bands which occurs near the limit of the spectrum. Only one distinct line was, in fact, certainly recognised on the photograph in this intermediate region, and by extrapolation from the hydrogen lines this was identified with the iron line 3440·8. This was subsequently used as a standard, in combination with H_γ (λ 4340·7) and H_θ (λ 3798·0), in the determination of the wave-lengths of the bands. The resulting wave-lengths are included in Table II; where they are compared with the positions assigned by Huggins and by Kohl, the latter being taken as the means of the two wave-lengths stated to represent the edges of each of the bands. The last column of the Table gives the strongest bands of ozone according to our measures.

Table II.—Ultra-violet Bands of Sirius compared with Ozone.

Spectrum of Sirius.					Ozone.		Remarks.
Huggins.	Kohl.		Fowler & Strutt.				
λ.	λ.	Int.	λ.	Int.	λ.	Int.	
3338	—	—	3337·2	2	3338·5	4	Kohl gives a "line" at 3337·5.
3311	—	—	3311·9	3b	3311·5	5b	
			3303·7	2	3304·1	3	
3278	3280·6	1	3285·0	1	3284·0	2	
			3279·8	5	3279·8	8b	
			3272·9	1	3272·0	3	
3254	—	—	3254·8	2	3255·5	5	Kohl gives a "line" at 3249·4.
			3249·7	5	3249·7	8	
3226	3224·8	2	3227·5	5b	3227·2	10	
			3220·0	5b	3221·5	10	
3199	3199·2	2	3201·7	4	3201·0	8b	There is possibly a metallic line in Sirius, about 3198.
			3194·8	4	3194·8	6	
	3176·6	1	3177·9	5b	3177·0	8b	These are only vaguely separated in Sirius.
			3172	2	3171·6	4	
	3158·2	—	3157	? 4b	3156·1	8	Estimates of intensity in star very uncertain on account of faintness of continuous spectrum.
			3138	? 4b	3137·4	10b	

The bands, as a whole, are more diffuse in the photograph of Sirius than in the laboratory spectra, and, making due allowance for the difficulties attending the measurement of band spectra, the agreement in the measured positions of the bands of Sirius with those of ozone may be considered very satisfactory. The proof of the identity of the two sets of bands, however, does not depend so much upon close coincidences in the measured positions of individual bands as upon a general agreement of the wave-lengths and intensities as a whole. This agreement is more convincingly demonstrated by the direct comparison of the spectrum of Sirius with that of ozone, as in fig. 3. A perfect correspondence of the two spectra in the region occupied by the bands is clearly indicated, there being no strong lines in the spectrum of Sirius to cause complication.

Ozone Absorption in the Solar Spectrum.

The presence of the Huggins group of bands in the spectrum of the low sun was indicated by numerous small-scale photographs taken during 1915. Measurements of the bands were rendered difficult by the superposition of metallic lines, but the general accordance of wave-lengths was sufficient to prove their identity with the bands appearing in Sirius. Kohl had previously noticed the bands in the sun, as we afterwards learned, but he apparently made no investigation of their varying intensity, and his list included three bands which were not indicated by him as appearing in the spectrum of Sirius.

Conclusive evidence that the bands are of telluric origin is furnished by photographs of the high and low sun, such as are reproduced in fig. 4. These have been selected from a series of 17 negatives obtained between noon and sunset on 1917, May 23, and show the spectrum corresponding to altitudes of the sun 55°, 30°, 10°, 4°, and 1°. It will be observed that as the sun's altitude is reduced there is a general advance of the complete absorption towards the red, accompanied by a gradual strengthening of the bands, so that the appearance of the spectrum about sunset is very different from that near noon. It follows that the bands are produced by absorption in our own atmosphere.

As in the case of Sirius, the identity of the bands with those of ozone is more convincingly demonstrated by direct comparison of the solar and experimental spectra than by attempts to prove exact agreement of wave-lengths. The spectrum of ozone given in the lowest strip of fig. 4 was obtained with a concentration closely corresponding to the maximum atmospheric absorption, and it will be seen that ozone accounts completely for the difference between the spectra of the high and low suns in the ultra-violet region.*

The foregoing investigation gives further substantial support to Hartley's suggestion that atmospheric ozone is the effective agency in fixing the limit towards the ultra-violet to which the solar spectrum can be observed. The extension of the complete absorption towards the red, and the successive appearances of bands of longer wave-lengths, as the sun's altitude becomes lower, correspond precisely with the phenomena observed in the experimental spectra as the quantity of absorbing ozone is increased.

* The apparent lack of exact coincidence about λ 3195 is due to an adjacent group of solar lines near the more refrangible edge of the corresponding band of ozone.

It may be that the recognition of these narrow absorption bands of ozone in the ultra-violet spectra of the sun and stars will facilitate investigations relating to atmospheric ozone, as the bands occur in a part of the spectrum which is easily photographed, and only a small spectrograph is necessary to show them.

The authors desire to record their appreciation of the kindness of Prof. Sampson in freely placing at their disposal the Edinburgh photograph of the spectrum of Sirius, which was the origin of the present investigation. They are also indebted to Mr. J. Brooksbank, B.Sc., for a number of photographs of the solar spectrum, and for assistance in preparing the plate for reproduction.

DESCRIPTION OF PLATE.

FIG. 1.—To illustrate the great absorption band of ozone in the ultra-violet.

(*a*) Cadmium spark, without ozone.
(*b*) Absorption due to 1·2 cm. dilute ozone.
(*c*) Absorption due to 3·5 cm. dilute ozone.
(*d*) Absorption due to 7·5 cm. dilute ozone.

FIG. 2.—To illustrate the advance of the great absorption band towards the red, and to show the appearance of the narrow bands at successively longer wave-lengths, as the thickness of absorbing ozone is increased. The source of light was burning magnesium, and λ 2852 appears as a reversed line.

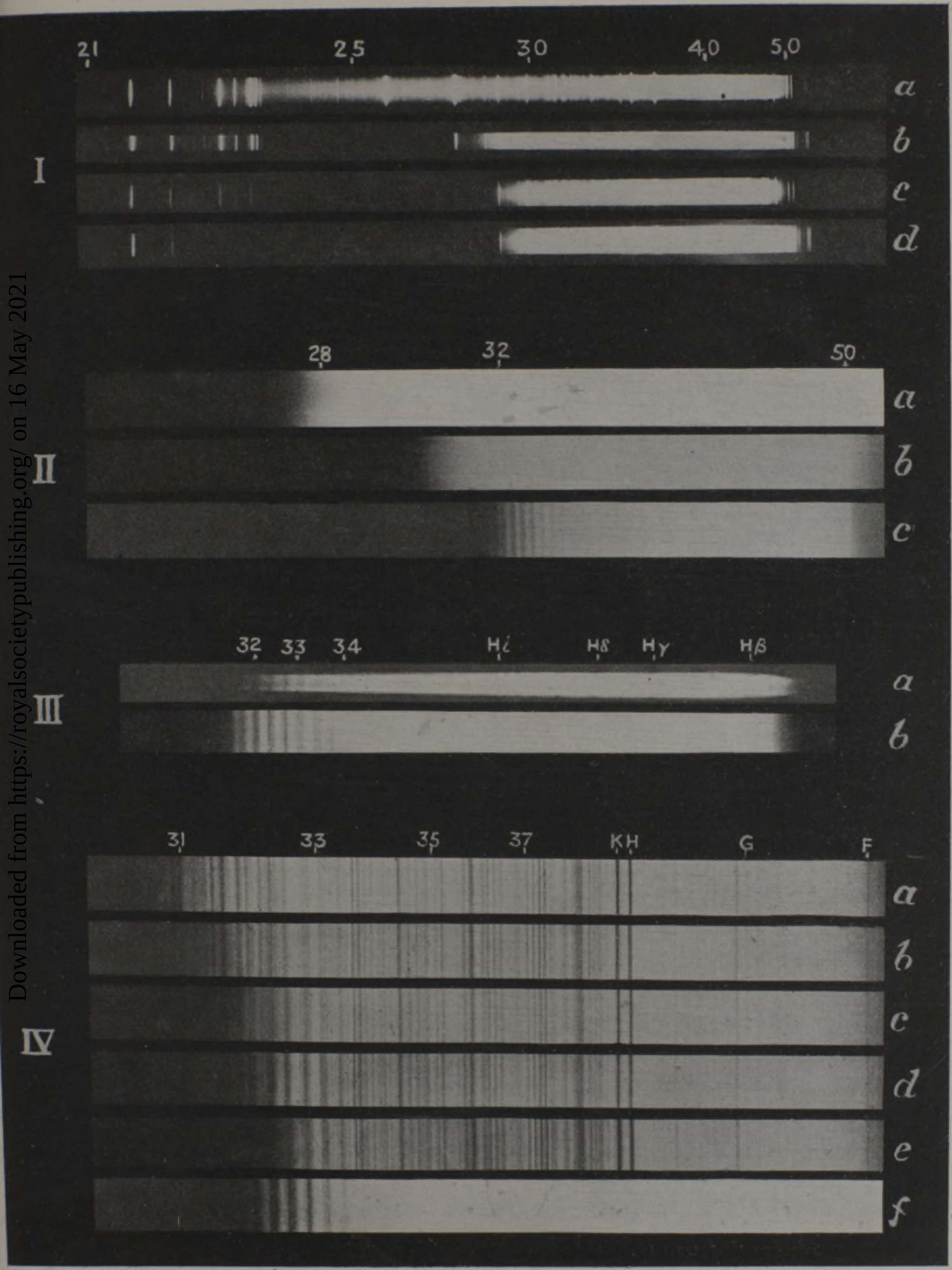
(*a*) 1 cm. of dilute ozone, showing faint bands from λ 2700 to λ 2840.
(*b*) 45 cm. of dilute ozone, showing stronger bands from λ 3000 to λ 3200.
(*c*) 175 cm. of dilute ozone, showing strong bands from λ 3150 to λ 3432.

FIG. 3.—The spectrum of Sirius compared with ozone.

(*a*) Spectrum of Sirius, photographed at the Royal Observatory, Edinburgh, on 1915, February 8; altitude of star about 15°.
(*b*) Absorption bands of ozone in the region λ 3150 to λ 3432.

FIG. 4.—Solar spectra, compared with ozone. Enlarged 5·7 times.

(*a*) Sun, altitude 55°
(*b*) Sun, altitude 30°
(*c*) Sun, altitude 10°
(*d*) Sun, altitude 4°
(*e*) Sun, altitude 1°
} 1917, May 23.
(*f*) Ozone absorption bands.


2,1
2,5
3,0
4,0
5,0
a
b
c
d
I
28
32
50
a
b
c
II
32
33
34
Hι
Hδ
Hγ
Hβ
a
b
III
31
33
35
37
K
H
G
F
a
b
c
d
e
f
IV

The Ultra-Violet Band of Ammonia, and its Occurrence in the Solar Spectrum.

By A. Fowler, F.R.S., and C. C. L. Gregory, B.A.

(Received December 15, 1917.)

(Abstract.)

A question of great interest in connection with the solar spectrum is that of the origin of the thousands of unidentified faint lines which were photographed and catalogued by Rowland. Some of these lines may possibly be identical with faint lines in metallic spectra which have not yet been completely tabulated, but in view of the presence of bands of cyanogen, carbon, and hydrocarbon, the possibility of the correspondence of most of them with band spectra of other substances should not be overlooked.

As a contribution to this inquiry, the present investigation was undertaken primarily in order to determine whether Group P in the ultra-violet region of the solar spectrum might not be mainly due to the presence of ammonia in the absorbing atmosphere of the sun. Ammonia was already known to give a remarkable band in this region, having its greatest intensity near λ 3360, but existing records of the component lines were inadequate for comparison with the solar tables. Photographs were accordingly taken with instruments of various dispersions, ranging up to that of the third order of a 10 feet concave grating, a copper arc in an atmosphere of ammonia being employed as the source in the latter case. In view of the unusual appearance of the band, an attempt has also been made to elucidate the chief features of its structure.

The chief ammonia band consists of a bright central maximum about λ 3360, a secondary maximum about λ 3371, and a number of lines, which are arranged in groups of three, extending to a considerable distance in both directions. The lines composing the two maxima are very closely crowded together and have been found to be arranged in series of ordinary type. The components of the groups of three are widely separated near the central maxima, but the intervals rapidly diminish and there is final coalescence at λ 3450 towards the red, and at λ 3287 towards the violet, where the lines fade out. The groups of three, however, are not symmetrical with respect to the central maxima, and they show marked peculiarities, so that they are very imperfectly represented by the formulæ usually employed for band spectra.

The comparison with the solar spectrum is considerably complicated by

the presence of lines of metallic origin, but there is abundant evidence that many of the fainter solar lines are due to ammonia. The most convincing proof of the presence of ammonia in the sun is perhaps afforded by the strongest parts of the central maximum, as indicated by the following extract from a table which is given in the paper :—

Ammonia.		Sun.			Remarks.
λ (Rowland scale).	Intensity.	λ Rowland.	Intensity.	Origin.	
3360·82	3	3360·828	0		Continuous background in both spectra.
60·72	3	60·741	0		
60·62	5	60·631	0		
		60·485	1	Cr	
60·45	8	60·444	2	Ni	Continuous background in both spectra.
60·33	3	60·345	0		
60·24	5	60·258	0		
60·18	10	60·181	2		
3360·08	4	3360·066	0		

It will be seen that there is a complete correspondence of the solar and laboratory spectra as regards these two clusters, except that the line 3360·44 in the sun may be slightly reinforced by a line which Rowland attributes to nickel, though it is not given as such by Exner and Haschek. The agreement is emphasised by the occurrence of patches of continuous background (dark in the sun) which are identical in the two spectra. The coincidences in the case of the central maximum, as a whole, are scarcely less striking, and it is clear that the solar Group P is largely due to ammonia.

There is also a sufficiently consistent representation of the groups of three, and of the lines composing the secondary maximum of the ammonia band. Of the 260 band-lines of ammonia in the region λ 3450 to λ 3286, there are 140 which correspond with previously unidentified faint lines of the solar spectrum. About 100 of the remaining lines are obscured by lines for which metallic origins have been found, or fall upon lines which are too strong in the sun to be assigned solely to ammonia, and the few which fail to appear in the sun are all of low intensity.

The Presence in the Solar Spectrum of the Water-vapour Band λ 3064.

By A. Fowler, F.R.S.

(Received December 15, 1917.)

The recent discovery of the ammonia band λ 3360 in the solar spectrum* suggested that additional solar lines might be identified by a search for other bands which are produced under generally similar conditions in laboratory experiments. In the first instance, comparison has been made with the water-vapour band λ 3064, which accompanies the ammonia band in the ammonia flame and in the arc in ammonia.

This band was discovered by Liveing and Dewar† in 1880, and independently, about the same time, by Huggins.‡ It was found by Liveing and Dewar that the band appeared in the flame of hydrogen or of hydrocarbons, and less strongly in the flames of non-hydrogenous gases, such as carbonic oxide and cyanogen, if burnt in moist air; it occurred also in the uncondensed discharge through moist hydrogen or other gases, but disappeared when the gas and apparatus were thoroughly dried, or when a large coil, with condenser, was the source of discharge. It was accordingly concluded by Liveing and Dewar that the spectrum in question was that of water-vapour, but they were careful to explain that in writing of this and other spectra which had been traced to compounds, they abstained from speculating upon "the particular molecular condition or stage of combination or decomposition which may give rise to such spectra." Subsequent work has likewise indicated that both hydrogen and oxygen are essential to the development of the spectrum under consideration, but the precise nature of the combination involved cannot yet be deduced from the spectroscopic evidence.

The band λ 3064 was afterwards found by Liveing and Dewar to be associated with others of lower intensity, extending as far as λ 4100 towards the red, and to λ 2268 in the ultra-violet. Extensive measures of the lines composing these bands were made by the same observers.§

The chief band was measured more completely by Meyerheim‖ in 1904, and by Grebe and Holtz* in 1912. The latter series of wave-lengths have been found to be sufficiently accurate for effective comparison with the solar tables of Rowland. The wave-lengths are given on the International scale, and the lines are classified in three orders of intensity, 3 indicating the brightest, and 1 the weakest lines. The head of the band is marked by a pair of lines at 3063·547 (2) and 3063·713 (3), from which point the measured lines extend on the red side to 3291·687 (1). Strong lines persist to a considerable distance from the head, but in the less refrangible part of the band, the lines become generally weak and relatively far apart.

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* Communicated to the Royal Society on December 15, 1917, by A. Fowler and C. C. L. Gregory.

† 'Proc. Roy. Soc.,' vol. 30, pp. 494, 580 (1880).

‡ 'Proc. Roy. Soc.,' vol. 30, p. 576 (1880).

§ 'Phil. Trans.,' vol. 179, p. 27 (1888).

‖ 'Zeitschr. f. Wiss. Phot.,' vol. 2, p. 131.

The result of the comparison is to prove that the band 3064 is quite strongly represented in the solar spectrum, and accounts for a large number of lines which were previously unidentified. It will suffice for the present purpose to give details relating to the brighter lines of the band, as in the appended Table. To facilitate comparison with the solar lines, the wave-lengths given by Grebe and Holtz have been reduced to Rowland's scale by the addition of the following corrections, derived from the curve given by Kayser† :—

Range of wave-lengths.	Correction from I.A. to Rowland.
3057—3072	+0·121
3072—3087	122
3087—3102	123
3102—3117	124
3117—3132	125
3132—3147	126
3147—3162	127
3162—3177	128
3177—3192	+0·129

The corrected wave-lengths are given in the first column of the Table. In Grebe and Holtz' list there are 53 lines which are classed as of intensity 3, but three of them are comparatively faint in my own photographs, and have therefore been omitted. As the scale of intensities adopted by Grebe and Holtz appears to be unduly restricted, my own estimates, on the basis of 6 for the strongest lines, are given in the second column of the Table. The following three columns show the wave-lengths, intensities, and origins of solar lines, as tabulated by Rowland. The sixth column indicates the difference "sun *minus* water-vapour," except in the case of near coincidences with metallic lines. The last column indicates the distances of the solar lines which are nearest to those which correspond to water-vapour.

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[*] 'Ann. d. Physik,' vol. 39, p. 1243.

[†] 'Handb. d. Spect.,' vol. 6, p. 890.

Water-vapour.		Sun (Rowland).			Sun *minus* w.v.	Next nearest solar line.
λ (G. and H.).	Intensity (F.).	λ.	Intensity.	Origin.		
3063 ·834	5	3063 ·836	2		+002	+076
64 ·307	5	64 ·323	2		+016	+152
67 ·354	4	67 ·369	8	Fe		
68 ·039	5	68 ·046	2		+007	−151
74 ·477	3	74 ·492	1		+015	+050
78 ·552	5	78 ·552	3	Fe		
80 ·084	5	80 ·086	4	Fe ?		
81 ·648	5	81 ·657	1		+009	−090
83 ·384	5	83 ·389	1		+005	+100
85 ·304	5	85 ·313	2		+009	+125
87 ·449	5	87 ·451	1		+002	+108
89 ·843	6	89 ·851	2		+008	+123
89 ·968	6	89 ·974	2		+006	−123
91 ·301	5	91 ·319	1N		+018	−142
91 ·473	5	91 ·477	1		+004	−158
92 ·506	5	92 ·509	1		+003	+070
92 ·898	5	{ 92 ·818	4	Al		
		92 ·957	1	Al		
94 ·729	5	94 ·732	2		+003	+098
95 ·452	5	95 ·453	3*		+001	+093
96 ·242	4	96 ·244	2		+002	−099
96 ·938	5	97 ·008	5	—, Mg		
98 ·698	5	98 ·693	2		−005	+132
99 ·524	5	99 ·523	1		−001	+157
3099 ·689	3	3099 ·680	0N		−009	+100
3101 ·343	4	3101 ·347	1		+004	+175
02 ·256	5	02 ·253	1		−003	+151
05 ·775	5	05 ·782	1		+007	−114
06 ·133	5	06 ·137	2		+004	−138
06 ·658	5	06 ·664	2	Zr		
12 ·187	5	12 ·183	2	Fe, Ti ?		
13 ·476	5	13 ·490	1		+014	+070
17 ·311	4	17 ·309	1		−002	+048
22 ·661	6	22 ·680	2		+019	+094
24 ·051	5	24 ·070	1		+019	+138
27 ·790	3	27 ·784	2d ?*		−006	+175
28 ·389	4	28 ·402	1		+013	+097
30 ·366	5	30 ·380	3	V		
34 ·451	5	34 ·451	1		000	+059
36 ·996	5	37 ·005	1		+009	+135
40 ·843	5	40 ·872	3	Co, —		
43 ·901	5	43 ·879	4	Ti		
45 ·633	3	45 ·641	0		+008	−157
47 ·562	5	47 ·562	1		000	+152
51 ·110	5	51 ·120	1		+010	+092
54 ·619	5	54 ·608	1	—, Fe		
58 ·628	4	58 ·635	0		+007	+112
62 ·004	4	62 ·014	0		+010	+051
66 ·445	4	66 ·447	0		+002	−080
69 ·718	3	69 ·727	0		+009	+137
3183 ·082	3	3183 ·101	3	Fe, Ni ?		

* Some other substance probably also involved.

Of the 50 lines included in the Table, it will be seen that, while 12 are obscured in the sun by closely adjacent metallic lines, the remaining lines show a very close agreement in wave-length with solar lines, and a sufficiently consistent correspondence of intensities. The average deviation of the 38 water-vapour lines from the corresponding solar lines, taken without regard to sign, is, in fact, only 0·007 Å., while the range is from +0·019 to −0·009. The differences are not too great to be considered as arising from errors in the two sets of measurements and uncertainty as to the corrections from the international to the Rowland scale. Moreover, the deviations are clearly to some extent systematic, as indicated by the preponderance of positive signs. From the last column of the Table, it results that the average distance of the next nearest solar lines is 0·111 Å., and there is consequently no reason to suppose that the coincidences are accidental.

The total number of lines in Grebe and Holtz' list is 257; 63 of them are approximately coincident with, and therefore obscured by, lines in the sun which are of metallic, or probable metallic, origins, according to Rowland. Five, which cannot be traced in the sun, although not masked by metallic lines, are too faint to appear in my own photographs or in Meyerheim's list, so that their apparent absence is of no significance. With very few exceptions, which require further investigation, all the remaining lines are closely coincident with solar lines, but it is possible that several of them are slightly too strong in the sun to be attributed solely to water-vapour, notwithstanding the close agreement in wave-lengths. At least 150 of the solar lines in the region of the λ 3064 band, however, may confidently be assigned exclusively to water-vapour. It is further probable that many additional solar lines will be traced to water-vapour when sufficiently accurate measures of the other bands become available for comparison.

Besides accounting for a large number of previously unidentified solar lines, the identification of the water-vapour band in the solar spectrum is of interest as furnishing further evidence of the existence of oxygen in the sun.

The Series Spectrum of Trebly-Ionised Silicon (*Si IV*).

By A. Fowler, F.R.S., Professor of Astrophysics, Imperial College, South Kensington.

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Introductory.

The investigation dealt with in the present paper forms part of a more extended inquiry into the various spectra of silicon which has been in progress during several years. The work was undertaken in the first instance in the hope of reaching a more complete physical explanation of the stellar spectra in which the different classes of silicon lines make their appearance. Lockyer and his assistants had already shown that certain lines, which successively appeared in laboratory experiments as the energy of excitation was increased, were correspondingly represented in the spectra of stars following each other in order of increasing temperature. Four groups of silicon lines were thus recognised, namely :—

Group I. λλ3905·8, 4103·2 (Arc lines).
Group II. λλ3853·9, 3856·1, 3862·7, 4128·1, 4131·1, 5042, 5057 (Spark lines).
Group III. λλ4552·8, 4568·0, 4574·9 } (Vacuum tubes).
Group IV. λλ4089·1, 4116·4 }

Lines of Group I occur in the solar spectrum, and in stars of types G and K; those of Group II are especially marked in stars of types F and A; while those of Groups III and IV occur in successively hotter stars of type B.

It seemed that the significance of the changes in the silicon spectrum might probably be better understood if the characteristics of the series including the different groups of lines could be ascertained. Bohr's theory had already given a completely satisfactory explanation of the change from the ordinary spectrum to the enhanced spectrum in the case of helium, and subsequent work by the present writer had shown that a similar explanation held for the enhanced (spark) spectra of the alkaline earth elements.* These investigations had shown that, in passing from arc to spark lines, the series constant was changed from Rydberg's N to 4N, and the theory indicated the possibility of other types of series in which the series constant might take the still higher values, 9N, 16N, and so on.† The stellar observations thus suggested silicon as a promising element in the search for these higher types of series. Stellar spectra, however, cannot be observed over a wide enough range for the investigation of series relationships, and more extended laboratory observations were therefore necessary.

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* 'Phil. Trans.,' A, vol. 214, p. 225 (1914).

† See, *e.g.*, A. Fowler, "Report on Series in Line Spectra," 'Physical Society,' pp. 65 and 164.

In the first instance, the observations were restricted to the region which could be studied with ordinary grating and quartz spectrographs, extending from about λ 6600 to λ 1854, and many additional lines were observed at each of the stages corresponding with Lockyer's groups. Series with 4N for the constant were definitely established for the Group II lines, and series with the constant 9N were strongly suggested by the additional observations of lines of Group III. Two further pairs of lines belonging to Group IV were also produced, but the three pairs were insufficient to permit any conclusion as to the value of the series constant in this case.

An extension of the observations into the Schumann region thus became essential for further progress, and such observations were made possible by a grant from the Government Grant Committee of the Royal Society for the purchase of a Hilger vacuum grating spectrograph. Up to the present time the work with this instrument has been restricted to the wave-lengths which are transmitted by fluorite, a plate of which covered the slit, but lines of critical importance for the purpose in view have been recorded.

The series systems of the four groups of lines have not yet been completely disentangled, but there is already sufficient evidence that the results are in general accord with Bohr's theory, and that the classification of silicon lines, which was first deduced by Lockyer from the behaviour of these lines in laboratory and stellar spectra, has a true physical basis. In accordance with the developments of Bohr's theory, the different groups appear to represent successive stages of ionisation of the silicon atoms, and the four groups may thus be designated—

Group I: Si I, or Si (neutral atoms).
Group II: Si II, or Si^+ (singly-charged atoms).
Group III: Si III, or Si^{++} (doubly-charged atoms).
Group IV: Si IV, or Si^{+++} (trebly-charged atoms).

The lines of Group I form a triplet system, in which, however, the regular triplets are not strongly developed. Those of Group II form a typical doublet system, those of Group III a second triplet system, and those of Group IV a second doublet system. The alternation of doublets and triplets is in precise agreement with the displacement law of Kossel and Sommerfeld, according to which the enhanced spectrum of an element should be of the same type as that of the arc spectrum of the element which precedes it in the periodic table.

Pending a further consideration of the series which characterise the lines of Groups I, II and III, the present communication gives an account of the chief observational results relating to the series lines of Group IV.

It should be noted that shortly before the completion of the present paper, the detection of series of aluminium lines having 9N for the series constant was announced by Paschen.* As giving an additional term of comparison, the consideration of Paschen's results in connection with the silicon series has added considerably to the interest of the present investigation.

Experimental Procedure.

The sources employed were the ordinary arc and spark between silicon electrodes and vacuum tubes containing chloride or fluoride of silicon, chiefly the latter. Sparks in an atmosphere of hydrogen, with and without self-induction in the secondary circuit, were also utilised in the case of the Schumann spectrograph. The strongest development of the lines of Si IV was obtained by passing strong condensed discharges through a quartz capillary tube in which the residual gas was oxygen at a very low pressure.

Quartz spectrographs were largely employed in the preliminary observations, but most of the wave-lengths finally adopted were deduced from photographs taken in the first-order spectrum of the 10-feet concave grating The Schumann spectrograph is provided with a 4-inch grating, ruled with 15,000 lines to the inch, and having a radius of 1 metre. The grating was specially ruled by Dr. Mackenzie of the Johns Hopkins University, with a view to its use in the region of short wave-lengths. Standards of reference in this region were provided by the work of Lyman, Millikan and Simeon, the positions of carbon lines given by the latter being especially valuable on account of the general occurrence of carbon impurities in the sources employed.

Numeration of Series Terms.

Of the two systems of numeration of series terms which have hitherto been chiefly in use, the system introduced by Rydberg has been adopted by Hicks† and the present writer,‡ while that of Ritz has been largely employed by Paschen and other German investigators. Following the development of the quantum theory of spectra, however, it would appear that neither the Rydberg nor the Ritz system is likely to be permanently adopted.

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* 'Ann. d. Phys.,' 1923. (The author is indebted to Prof. Paschen for an advance proof of this paper.)

† 'The Analysis of Spectra,' Camb. Univ. Press, 1922.

‡ "Report on Series in Line Spectra," 'Phys. Soc. London,' 1922.

In the Ritz system, the smallest term numbers for the sharp, principal, diffuse, and fundamental (or Bergmann) sequences are respectively 1,* 2, 3, 4, and the work of Sommerfeld† has suggested that these represent the smallest azimuthal quantum numbers—and, therefore, the smallest total quantum numbers—associated with the respective sequences.

In the new system of numeration introduced by Bohr‡ the first total quantum number increases from row to row in the periodic table of the elements, being, for example, two for lithium, three for sodium, and so on, up to six for cæsium. The spectrum being supposed to be produced by the orbital transitions of one of the outermost electrons, the total quantum numbers are the sums of the azimuthal and radial quantum numbers which further characterise the orbits. The azimuthal components are the respective minimum values assigned by Ritz, and while the azimuthal quantum remains the same for a given sequence of terms, the radial component ranges in value from that required to complete the first total quantum number up to infinity. Thus, since the azimuthal quantum number associated with the sharp sequence of terms is 1, the corresponding first *s* orbit for sodium is more completely represented by 3_1. Similarly, the first *p* and *d* orbits of sodium are indicated by 3_2, 3_3; and, in general, the symbol m_k indicates that the total quantum number is *m* and the azimuthal component *k*. In the consideration of series, however, the azimuthal component of the total quantum number is sufficiently indicated by the associated term symbols *s*, *p*, *d*, *f*.

It will be observed that while the Rydberg or Ritz numbers are the same for corresponding series of all elements, the Bohr system assigns different numbers to corresponding series terms, even of elements belonging to the same chemical group. Taking sodium as the most useful example for the present purpose, the three systems may be compared as follows:—

	For all spectra.		For Na—Bohr.
	Ritz.	Rydberg.	
Sharp (*s*)	1, 2, ...	1, 2, ...	3, 4, ... [3_1, 4_1, ...]
Principal (*p*)	2, 3, ...	1, 2, ...	3, 4, ... [3_2, 4_2, ...]
Diffuse (*d*)	3, 4, ...	2, 3, ...	3, 4, ... [3_3, 4_3, ...]
Fundamental (*f*)	4, 5, ...	3, 4, ...	4, 5, ... [4_4, 5_4, ...]

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* Ritz assigned 1·5 *s* to the first *s* term, but this has been generally abandoned in favour of 1 *s*.

† 'Atombau und Spektral-linien,' 2nd edition, p. 278 (1921).

‡ 'The Theory of Spectra and Atomic Constitution,' p. 97 (Camb. Univ. Press, 1922).

The well-known series formula of Ritz in the form

$$\nu = \mathrm{A} - \frac{\mathrm{N}}{[m+\mu+\alpha(\mathrm{A}-\nu)]^2}$$

is evidently adapted to any system of numeration, since the order number m and the constant μ are not separately determinable, so that any modification of m for a given term may be compensated by a corresponding adjustment of μ.

The more convenient Hicks formula,

$$\nu = \mathrm{A} - \frac{\mathrm{N}}{[m+\mu+\alpha/m]^2},$$

generally represents series with no less accuracy than the Ritz formula, provided that the terms are numbered on the Rydberg system; it requires to be re-written if a different numeration be adopted. Thus, if the first term of a sequence represented by 1 s on the Rydberg system is to be designated 3 s, the constant μ must be replaced by μ' $(= \mu - 2)$, and the term formula would become

$$ms = \frac{\mathrm{N}}{[m-\mu'+\alpha/(m-2)]^2},$$

and so on.

At the present transition stage, it has not seemed necessary to sacrifice the simplicity of the Hicks formula and the Rydberg order-numbers in the investigation of the series of Si IV, but the new numeration will be duly indicated in the collected results.

The Series System of Si IV (Si^{+++}).

As suggested by the displacement law of Kossel and Sommerfeld, the series of Si IV have been found to consist of doublets and to have a general resemblance to the series of neutral sodium, Na I. The series corresponding with the best known series of Na I, however, lie in the extreme ultra-violet, in consequence of the greater value of the series constant, while those which occur in the ordinary region of observations in Si IV correspond with secondary series of Na I, which occur in the infra-red and have only been partially observed.

As in the series at previous stages of ionisation, the intensities in the series of Si IV appear to degrade very rapidly with increasing order number, so that the number of lines available for the calculation of constants is at present somewhat restricted. In the first instance, it was assumed that the constant for these series was sixteen times that for hydrogen, namely, 16 N = 1,754,852. Then, taking the stronger components of the secondary pairs, which have a separation $\Delta\nu = 162$, the data and Rydberg formulæ are as follows:—

$$\left.\begin{aligned}\sigma_1(2) &= 2\pi_1 - 2\sigma = -24450^* \\ \sigma_1(3) &= 2\pi_1 - 3\sigma = 46989\end{aligned}\right\} \sigma_1(m) = 146{,}112 - \frac{16\,\mathrm{N}}{[m+1\cdot207606]^2},$$

$$\left.\begin{aligned}\delta_1(2) &= 2\pi_1 - 2\delta = -58050^* \\ \delta_1(3) &= 2\pi_1 - 3\delta = 31579\end{aligned}\right\} \delta_1(m) = 144{,}374 - \frac{16\,\mathrm{N}}{[m+0\cdot944363]^2}.$$

The two limits are in as close agreement as could be expected from the use of the simple Rydberg formula, and the agreement may be taken as a provisional justification of the use of 16 N for the series constant. The formula for the sharp series may be supposed, as is usually the case, to be the more exact, and it may therefore be used with some confidence to extrapolate to the term $1\,\sigma$, and to calculate an approximate formula for the associated principal series. Thus—

$$1\sigma = \frac{16\mathrm{N}}{[2\cdot207606]^2} = 360082,$$

$$2\pi_1 = 146112 = \frac{16\mathrm{N}}{[3\cdot465606]^2},$$

$$2\pi_2 = 146112 + 162 = \frac{16\mathrm{N}}{[3\cdot463687]^2},$$

$$\pi_1(m) = 1\sigma - m\pi_1 = 360082 - \frac{16\,\mathrm{N}}{[m+1\cdot465606]^2},$$

$$\pi_2(m) = 1\sigma - m\pi_2 = 360082 - \frac{16\,\mathrm{N}}{[m+1\cdot463687]^2}.$$

From these there results for the first principal pair :—

$$\pi_1(1) = 1\sigma - 1\pi_1 = 360082 - 288667 = 71415,$$

$$\pi_2(1) = 1\sigma - 1\pi_2 = 360082 - 289117 = 70965,$$

$$\Delta\nu = 450.$$

There is actually a strong pair of Si IV lines, classified as such from their behaviour under varying experimental conditions, the components of which are as close to these positions as can be expected, and have an appropriate separation. They were noted by Millikan, Bowen, and Sawyer† in their observations of the "vacuum spark" spectrum of carbon, and marked "Si, Ca?". Their silicon origin is confirmed by their behaviour in the present series of observations. The wave-lengths are given by Millikan as 1402·9 and 1393·9, the corresponding wave-numbers being 71280, 71740, giving $\Delta\nu = 460$. These may be accepted with confidence as the leading pair of the first principal series; the second member would be far outside the region of observation covered by the present investigation.

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* It should be noted that two of the pairs have their stronger components on the more refrangible side, and must accordingly be written with a negative sign. The use of Greek letters is intended to indicate that the lines belong to a doublet system.

† 'Astrophys. Jour.,' vol. 53, p. 159 (1921).

Lines possibly belonging to fundamental series were next considered. The corresponding terms in other spectra are in all cases rather larger than $N/(m+1)^2$, and here we should expect $3\phi > 16N/4^2$, say 111,000, and $4\phi > 16N/5^2$, say 71,000. The limit will be 2δ or 3δ, which may be evaluated thus:—

$$2\delta = 2\pi_1 - \delta_1(2) = 146112 + 58050 = 204162,$$

$$3\delta = 2\pi_1 - \delta_1(3) = 146112 - 31579 = 114533,$$

from which

$$2\delta - 3\phi = 204162 - 110000 = 94162,$$

$$3\delta - 4\phi = 114533 - 71000 = 43533.$$

The first lies beyond the range of the present observations, but a strong line in the carbon spark at λ 1066·0, $\nu = 93{,}809$, has been marked "Si ?" by Millikan, and very probably represents the calculated line. Simeon,* who appears to have used purer samples of carbon than Millikan, gives only a very faint line at λ 1066·3, $\nu = 93782$, which makes the silicon origin more probable. There is also a strong line of Si IV at λ 2287·08, $\nu = 43710$, which corresponds sufficiently with the second calculated line.

The allocation of the lines to the different series and the use of 16N as the series constant for Si IV is perhaps sufficiently justified by the above considerations, but further evidence is afforded by an independent calculation of the series constant from the data for the $\sigma\pi$ lines. Thus, we have

$$\nu_1 = \frac{B}{(1+s)^2} - \frac{B}{(1+p)^2} = 71740,$$

$$\nu_2 = \frac{B}{(2+s)^2} - \frac{B}{(2+p)^2} = 24450,$$

$$\nu_3 = \frac{B}{(3+s)^2} - \frac{B}{(2+p)^2} = -46989.$$

By assuming approximate values of B, *s*, and *p*, and forming three linear equations of the type

$$\Delta\nu = \Delta B\left[\frac{1}{(1+s)^2} - \frac{1}{(1+p)^2}\right] - \frac{2B}{(1+s)^3}\,.\,\Delta s + \frac{2B}{(1+p)^3}\,.\,\Delta p,$$

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* 'Roy. Soc. Proc.,' A, vol. 102, p. 490 (1923).

corrections to the assumed values were calculated. In this way it was found that for the three lines in question

$$B = 1{,}737{,}965, \qquad s = 1{\cdot}195987, \qquad p = 1{\cdot}453746.$$

The value of B thus determined is equivalent to 15·846N, which is nearer to 16N than could have been expected, since the data at present available are insufficient to permit the use of correcting terms in the Rydberg formulæ employed. In the subsequent calculations, 16N has therefore been adopted as the series constant for the doublet system of Si IV.

It remains to calculate the most probable values of the series terms from the best available data, namely,

$1\pi_1 - 1\sigma = -71740,$
$2\pi_1 - 2\sigma = -24450,$
$2\pi_1 - 3\sigma = 46989,$
$2\pi_1 - 2\delta = -58050,$
$2\pi_1 - 3\delta = 31579,$
$3\pi_1 - 3\delta = -26571.$

$2\delta - 3\phi = 93782,$
$3\delta - 4\phi = 43710,$
$3\delta - 5\phi = 65212,$
$4\delta - 5\phi = 23732,$
$4\delta - 6\phi = 36702.$

The ϕ terms appear to be the most suitable for computation, on account of their greater number, and by various combinations of the above we find the following values for their consecutive differences :—

$$3\phi - 4\phi = 39557,$$
$$4\phi - 5\phi = 21502,$$
$$5\phi - 6\phi = 12970.$$

A solution by the method of least squares gives the formula

$$m\phi = \frac{16N}{[m + 0{\cdot}988903 + 0{\cdot}019900/m]^2}$$

from which we find $3\phi = 109923{\cdot}4$; $4\phi = 70366{\cdot}3$; $5\phi = 48861{\cdot}7$; $6\phi = 35893{\cdot}1$. These in turn lead to values for the δ terms, and thence, in succession, to the π_1 and σ terms. For example,

$$2\delta = 109923 + 93782 = 203705.$$

From the $2\pi_1$, $3\pi_1$ terms, and the 2σ, 3σ terms, the following formulæ have been derived :—

$$m\pi_1 = \frac{16N}{[m + 1{\cdot}492563 - 0{\cdot}043080/m]^2},$$

$$m\sigma = \frac{16N}{[m + 1{\cdot}228166 - 0{\cdot}032538/m]^2}.$$

Extrapolations give $1\pi_1 = 292477$, and $1\sigma = 364018$. The difference is 71541, which is as close to the observed line 71740 as can be expected. As there is no reason to suppose one of the terms to be more correct than the other, one has been increased, and the other diminished by an equal amount, so as to make the difference equal to the wave-number of the line to which it corresponds. Thus the adopted values are $1\sigma = 364117$; $1\pi_1 = 292377$. The satisfactory values of the extrapolated terms indicate that the formulæ will give values for additional terms which cannot be greatly in error.

For the calculation of additional terms of the diffuse series, the following formula has been derived from the 3δ and 4δ terms:—

$$m\delta = \frac{16\mathrm{N}}{[m+0\cdot900071+0\cdot066204/m]^2}.$$

Extrapolation gives $2\delta = 203969$, which is in as close agreement as is to be expected with the value 203705 derived above. Smaller terms calculated from the formula will, therefore, be not far from correct.

Finally, the first three π_2 terms have been derived by adding the observed separations of the corresponding pairs to the respective π_1 terms. The $2\pi_2$ and $3\pi_2$ values then give the following formula for the calculation of additional π_2 terms:—

$$m\pi_2 = \frac{16\mathrm{N}}{[m+1\cdot490667-0\cdot043146/m]^2}.$$

So far, only the four most generally recognised types of series have been considered, namely, the sharp, principal, diffuse, and fundamental. The occurrence of series with a constant which is a multiple of that for hydrogen, however, has made it possible to observe additional types which were not identified in the earlier work on series, in consequence of their occurrence in the extreme infra-red. An example of such a new type of series was provided by the author's observations of Mg II. These included a series which was designated $3\phi-m\phi$, but it was pointed out that this combination did not agree with the observed values within the limits of experimental errors.* Bohr, however, has shown† that the disagreement disappears on the introduction of a fifth series of stationary states, which must be supposed to exist according to the general theory. The series in question thus becomes $3\phi-m\phi'$, where the new set of terms $m\phi'$ differ only slightly from the terms $m\phi$. The series $3\phi-m\phi'$ has been identified by Paschen in Al III, and it is also represented in Si IV. A sixth type of series, $4\phi'-m\phi''$, which has been similarly recognised by Paschen in Al III, and thence in Na I, is also represented in Si IV. In Si IV, however, like other series, these higher series are only represented by their earliest members. The fifth and sixth types of series have been called by Paschen the Super-Bergmann (Über-Bergmann), and Super-Super-Bergmann (Über-Über-Bergmann) series.

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* 'Phil. Trans.,' A, vol. 214, p. 253 (1914).

† 'The Quantum Theory of Line Spectra,' Part III, Copenhagen, 1922.

The terms which have been evaluated in these various ways are summarised in Table I, those depending solely upon formulæ being enclosed in brackets. The Rydberg numeration of the terms is indicated on the left, and the new Bohr numeration on the right. While preference should probably be given to the latter, it seems desirable, for the present, to indicate also the Rydberg numeration, in order to facilitate comparison with existing Tables of series; in what follows, the Rydberg numbers will be enclosed in brackets for distinction.

Table I.—The Series Terms of Si IV.

Rydberg numbers.	σ.	π_1.	π_2.	δ.	ϕ.	ϕ'.	ϕ''.	Bohr numbers.
(1)	364117	292377	292837					
				203705				3
(2)	170105	145655	145817					
				114076	109923			4
(3)	98666	87505	87580					
				72594	70366	70213		5
(4)	[64401]	[58397]	[58438]					
				[50186]	48862	48788	48733	6
(5)	[45319]	[41741]	[41766]					
				[36741]	35893	35835	[35800]	7
(6)	[33638]	[31319]	[31335]					
				[28050]	[27476]			8

The largest term, it will be observed, is the (1) σ or 3 σ (Bohr) term, which may be utilised in the usual way to determine the energy required to remove the fourth of the outermost electrons from the silicon atom when three of them have already been expelled. The ionisation potential thus deduced is 44·95 volts.

The lines included in the present discussion are collected in Table II, which is arranged in accordance with the plan adopted in the author's Report on Series, to which reference has already been made.

In Mg II and Al III the δ terms have two values, differing slightly, so that lines involving the earlier terms are very close doublets, consisting of a chief line and satellite. In Si IV the first diffuse pair is in the far ultra-violet, so that such duplication cannot be directly observed; the related line of the fundamental series (λ 1066) is also in the far ultra-violet. No indication of a satellite has been noted in the measurements of the first member of the second diffuse series (λ 3165), but the line λ 2287, which is $4\,(3)\,\delta - 5\,(4)\,\phi$, shows signs of resolution on some of the photographs. The term $5\,(4)\,\phi$

Table II.—Series of Si IV.

1st Principal. $3\,(1)\,\sigma - m\pi$.
$3\,(1)\,\sigma = 364117$.

Int.	ν.	$\Delta\nu$.	m.	$m\pi_{1,2}$.
·9 (10) ·9 (8)	71740 71280	460	B R 3 (1)	292377 292837
·75] ·09]	218462 218300	162	4 (2)	145655 145817

1st Sharp. $3\,(1)\,\pi - m\sigma$.
$3\,(1)\,\pi_1 = 292377$; $3\,(1)\,\pi_2 = 292837$.

Int.	ν.	$\Delta\nu$.	m.	$m\sigma$.
·9 (10) ·9 (8)	71740 71280	460	B R 3 (1)	364117
·85] ·78]	[122272] [122732]	460	4 (2)	170105

1st Diffuse. $3\,(1)\,\pi - m\delta$.
$3\,(1)\,\pi_1 = 292377$; $3\,(1)\,\pi_2 = 292837$.

Int.	ν.	$\Delta\nu$.	m.	$m\delta$.
27 ·75] 21 ·93]	[88672] [89132]	460	B R 3 (2)	203705
60 ·85] 59 ·41]	[178301] [178761]	460	4 (3)	114076

1st Fundamental. $3\,(2)\,\delta - m\phi$.
$3\,(2)\,\delta = 203705$.

Int.	ν.	$\Delta\nu$.	m.	$m\phi$.
*16 ·3 (8)	93782	—	B R 4 (3)	109923
9 ·97]	[133339]	—	5 (4)	70366

2nd Principal. $4\,(2)\,\sigma - m\pi$.
$4\,(2)\,\sigma = 170105$.

λ, Int.	ν.	$\Delta\nu$.	m.	$m\pi_{1,2}$.
4088 ·863 (10) 4116 ·104 (8)	24449 ·80 24287 ·99	162 ·10	B R 4 (2)	145655 145817
[1210 ·65] [1211 ·75]	[82600] [82525]	75	5 (3)	87505 87580
[859 ·25] [859 ·52]	[111708] [111667]	41	6 (4)	[58397] [58438]

2nd Sharp. $4\,(2)\,\pi - m\sigma$.
$4\,(2)\,\pi_1 = 145655$; $4\,(2)\,\pi_2 = 145817$.

λ, Int.	ν.	$\Delta\nu$.	m.	$m\sigma$.
−4088 ·863 (10) −4116 ·104 (8)	−24449 ·80 −24287 ·99	162 ·10	B R 4 (2)	170105
2127 ·48 (4) 2120 ·19 (3)	46989 ·05 47150 ·62	161 ·57	5 (3)	98666
[1230 ·71] [1228 ·26]	81254 81416	162	6 (4)	64401

2nd Diffuse. $4\,(2)\,\pi - m\delta$.
$4\,(2)\,\pi_1 = 145655$; $4\,(2)\,\pi_2 = 145817$.

λ, Int.	ν.	$\Delta\nu$.	m.	$m\delta$.
−1722 ·7 (5) −1727 ·4 (4)	−58050 −57888	162	B R 3 (2)	203705
3165 ·72 (8) 3149 ·56 (6)	31579 ·28 31741 ·30	162 ·02	4 (3)	114076
[1368 ·72] [1365 ·69]	[73061] [73223]	162	5 (4)	72594

* N within range of present observations, but given by Millikan as Si, Ca ? in carbon spark ; Simeon's λ adopted.

Table II—(*contd.*).

2nd Fundamental. $4\,(3)\,\delta - m\phi$.
$4\,(3)\,\delta = 114076$.

λ, Int.	ν.	Δν.	*m.*	$m\phi$.
			B R	
*2287 ·08 (10)	43710 ·37	—	5 (4)	70366
†1533 ·47	65212	—	6 (5)	48862
[1279 ·05]	[78183]	—	7 (6)	35893

3rd Fundamental. $5\,(4)\,\delta - m\phi$.
$5\,(4)\,\delta = 72594$.

λ, Int.	ν.	Δν.	*m.*	$m\phi$.
			B R	
4212 ·44 (3)	23732 ·43	—	6 (5)	48862
2723 ·82 (1)	36702 ·30	—	7 (6)	35892

Series $4\,(3)\,\phi - m\phi'$.
$4\,(3)\,\phi = 109923$.

λ, Int.	ν.	Δν.	*m.*	$m\phi'$.
			B R	
‡2517 ·52 (5)	39709 ·67	1 ·26	5 (4)	70213
	[61143]	—	6 (5)	48780

Series $5\,(4)\,\phi - m\phi'$.
$5\,(4)\,\phi = 70366$.

λ, Int.	ν.	Δν.	*m.*	$m\phi'$.
			B R	
4631 ·38 (3*n*)	21585 ·80	—	6 (5)	48780
2895 ·13 (1)	34530 ·67	—	7 (6)	35835

Series $5\,(4)\,\phi' - m\phi''$.
$5\,(4)\,\phi' = 70213$.

λ, Int.	ν.	Δν.	*m.*	$m\phi''$.
			B R	
4654 ·14 (4*n*)	21480 ·25	—	6 (5)	48733

Combinations.

λ, Int.	ν.	ν, calculated.
3762 ·41 (4)	26571 ·18	$4\,(3)\,\delta - 5\,(3)\,\pi_1 = 26571$
3773 ·13 (3)	26495 ·69	$4\,(3)\,\delta - 5\,(3)\,\pi_2 = 26496$
1796 ·1 (1)	55676	$4\,(3)\,\delta - 6\,(4)\,\pi_1 = 55679$
1797 ·5 (0)	55633	$4\,(3)\,\delta - 6\,(4)\,\pi_2 = 55638$

* Probably a very close pair.
† Coincident with a line of Si II.
‡ This is a close pair; λλ 2517 ·56, 2517 ·48 ; νν 39709 ·04, 39710 ·30.

therefore appears to have two values. The line $4\,(3)\,\phi - 5\,(4)\,\phi'$ (λ 2517), which has been definitely resolved into two components, with a separation $\Delta\nu = 1{\cdot}3$, similarly suggests two close values for the term $4\,(3)\,\phi$ It has not been thought desirable to complicate the Table with these details.

Numerous faint lines, which have appeared under conditions favourable to the development of lines of Si IV, have not yet been classified. It is possible that some of them may form part of a fifth spectrum of silicon, having a general resemblance to the spectrum of neon.

Comparison of Si IV, Al III, Mg II, and Na I.

The foregoing data provide conclusive evidence that the lines under consideration form part of a system of series having 16N for the series constant.

In accordance with Bohr's theory, the sixteenfold value is to be interpreted as meaning that the atoms which give these lines have lost three electrons. The atomic number of silicon is fourteen; the two innermost electrons are in 1-quantum orbits, eight are in 2-quanta orbits, and four are in 3-quanta orbits. When three of the outermost electrons have been removed, the remaining eleven are arranged as in the neutral atom of sodium (Na I), the singly-ionised atom of magnesium (Mg II), and the doubly-ionised atom of aluminium (Al III). Including Paschen's recent work on Al III, and the writer's previous investigation of Mg II, it is thus possible to compare the spectra of four different atoms, in which the number and distribution of the external electrons are identical, while the nuclei differ in charge and mass. As the only known effect of varying mass of the nucleus is to produce small changes in the series constant, it would seem that the differences in the four spectra are to be attributed mainly to differences in the nuclear charges, or to differences in the net charges of the atoms as a whole with respect to the electron which produces the spectrum by its transitions.

The Doublet Separations.—One obvious effect of increased nuclear charge is to produce a wider separation of the doublets, as will be seen from the following data:—

	Na I.	Mg II.	Al III.	Si IV.
Atomic weight	23·0	24·32	27·1	28·3
Nuclear charge..........................	11	12	13	14
Net charge of atom	1	2	3	4
Doublet separation	17·18	91·55	238	460

For the elements in the same vertical column of the periodic Table, as was found by Rydberg and by Kayser and Runge, there is a general increase in the doublet or triplet separations in approximate proportion to the squares of the atomic weights, but this relation is far from being exact. Other attempts have been made to correlate the separations with the atomic weights, or atomic numbers, but no exact relation has been discovered. Much greater regularity is shown, however, by the values of $\Delta\nu$ for the four atoms under consideration. If the $\Delta\nu$ be plotted against the respective nuclear charges, the points are found to lie on a smooth curve, and, similarly, if the logarithms of the two quantities are plotted. There is, however, no such regularity when the separations are plotted against the atomic weights.

The regularity is perhaps best shown by comparing the separations with the squares of the net charges of the four atoms with respect to the disturbed electron. The points then lie nearly on a straight line, but there is a definite curvature, so that the data may be represented by a formula of the type

$$\Delta\nu = 7{\cdot}5 + 36{\cdot}9\,(n - 0{\cdot}492)^2,$$

where $\Delta\nu$ is the separation, and n the corresponding net charge, with values ranging from 1 to 4. The residuals, observed *minus* calculated values, are +0·06, +0·08, −1·6 and −1·7, but it should be noted that the last two values of $\Delta\nu$ are subject to possible errors of a few units in consequence of the fact that errors of wave-length are multiplied by large factors in correcting to wave-numbers.

Corresponding Lines.—As already pointed out, one of the chief effects of an increase in the value of the series constant is to displace the spectrum as a whole towards the region of shorter wave-lengths. Thus the main series of Si IV which correspond with the familiar series of Na I are in the extreme ultra-violet, and only the earlier members of the secondary series lie within the ordinary region of observation with gratings and quartz spectrographs. This is indicated by the data already given, but it will be of interest to compare the positions of the leading lines in the four spectra, as in Table III.

Table III.—Comparison of Chief Lines.

		Na I.	Mg II.	Al III.	Si IV.
Principal 3 (1) σ—3 (1) π_1	λ	5889·9	2795·5	1854·7	1393·9
	ν	16973	35761	53918	71740
Diffuse 3 (1) π_1—3 (2) δ	λ	8194·8	2797·9	1611·9	[1127·7]
	ν	12199	35729	62037	[88672]
Sharp 3 (1) π_1—4 (2) σ	λ	11404	2936·5	1384·2	[817·8]
	ν	8766	34044	72244	[122272]
Fundamental 3 (2) δ—4 (3) ϕ	λ	18459	4481·3	1935·8	1066·3
	ν	5416	22309	51657	93782
4 (3) ϕ—5 (4) ϕ'	λ	40449	[10089]	4479·9	2517·5
	ν	2471·6	[9909]	22315	39710
5 (4) ϕ'—6 (5) ϕ''	λ	7·443 μ	—	[8276·1]	4654·1
	ν	1343·2	—	[12079]	21480

The figures in brackets are calculated positions, the actual lines not having been observed.

The displacement of corresponding lines towards the region of shorter wave-lengths in passing from Na I to Si IV is very clearly indicated by the figures quoted. The displacement, moreover, appears to be very regular throughout, for if corresponding lines are plotted against atomic numbers, or numbers increasing by unity, the points lie on smooth curves.

Comparison of Series Terms.—It is of further interest to compare the series terms of the four atoms of similar electron structure which are under consideration, as in Table IV.

Table IV.—Comparison of Series Terms.

Bohr numbers ………		3.	4.	5.	6.	7.
Rydberg numbers …		(1).	(2).	(3).	(4).	(5).
$m\sigma$ ($k=1$)	Na I …	41449·0	15709·5	8248·3	5077·3	3437·3
	Mg II …	30316·9	12865·5	7120·3	4517·3	3120·7
	Al III …	25493·3	11475·2	6533·7	[4216]	
	Si IV …	22757·3	10631·6	6166·6	[4025]	
$m\pi_1$ ($k=2$)	Na I …	24475·7	11176·1	6406·3	4151·3	
	Mg II …	21376·6	10154·0	5949·6	3909·2	
	Al III …	19502·4	9525·3	5663·3	[3756]	
	Si IV …	18273·6	9103·4	[5469]	[3650]	
Rydberg numbers …		(2).	(3).	(4).	(5).	(6).
$m\delta$ ($k=3$)	Na I …	12276·2	6900·4	4412·5	3061·9	2248·6
	Mg II …	12444·2	6988·8	4461·6	3091·6	2267·4
	Al III …	12609·4	7072·7	4507·1	3118·4	2284·3
	Si IV …	12731·6	7129·8	4537·1	[3137]	[2296]
$m\phi$ ($k=4$)	Na I …	—	6860·4	4390·4	[3042]	
	Mg II …	—	6866·9	4394·3	3051·2	2241·4
	Al III …	—	6869·7	4396·6	3052·2	2242·1
	Si IV …	—	6870·2	4397·9	3053·9	2243·3

As in Paschen's comparison of Na I, Mg II and Al III, the actual terms have been divided by 1^2, 2^2, 3^2 and 4^2 respectively. For Al III Paschen used the constant 9×109735, and in order to make the terms more directly comparable with those of the other elements, the Al III terms have been re-determined with the hydrogen constant. The Al III terms given in Table IV are 1·62 lower than the values given by Paschen, but the correction is of little importance except as regards the ϕ terms.

It will be observed that while the σ and π terms diminish regularly in passing from Na I to Si IV, the δ and ϕ terms become greater. When the corresponding first sharp, principal, or diffuse terms are plotted against the atomic numbers, or ordinates increasing by unity, the points lie on smooth curves, so that the regularity is much greater than appears in a similar comparison of terms of elements of the same chemical group, such as the alkali metals. No simple expressions representing the changes in the term values in the four spectra, however, have yet been found.

Quantum Defect.—It may be of further interest to compare some of the series terms of the four spectra in a different manner. If a series term be expressed in the form $B/(m-q)^2$, where m is the corresponding total quantum number according to Bohr's system, and B the appropriate series constant, q represents what has been called the "quantum defect."* This varies from term to term in the same series, and from series to series, according to the effective shielding of the nucleus by the surrounding electrons with respect to the different orbits occupied by the electron which produces the spectrum by its transitions. Some of the values of q are given in Table V.

Table V.—Quantum Defect.

	Na I.	Mg II.	Al III.	Si IV.
3σ	1·373320	1·097992	0·925815	0·804671
4σ	1·357718	1·080247	0·908424	0·788103
5σ	1·353479	1·075257	0·902851	0·782681
$3\pi_1$	0·883150	0·734880	0·630142	0·550099
$4\pi_1$	0·867331	0·713442	0·608280	0·528977
$5\pi_1$	0·862334	0·706451	0·600954	0·521769
3δ	0·010980	0·031232	0·050735	0·064957
4δ	0·013196	0·038514	0·062067	0·077860
5δ	0·014375	0·041890	0·066991	0·083343
4ϕ	0·001596	0·003485	0·004315	0·004456
5ϕ	0·001845	0·004079	0·005050	0·006112

In computing the values for Al III, the terms given by Paschen have been diminished by 14·6, in order to reduce them to the hydrogen constant which has been adopted for the other three spectra. As in the previous comparisons, corresponding figures for the four spectra exhibit remarkable regularity, and will doubtless be of value in theoretical discussions.

Summary.

Numerous new lines of silicon have been observed and have been classified in four groups, in extension of the groupings made by Lockyer in connection with stellar spectra. The four groups represent successive stages of ionisation, and have been designated Si I, Si II, Si III and Si IV. The spectra consist alternately of triplets and doublets, and the series constant has successive values N, 4N, 9N and 16N.

The present paper deals with the series of Si IV, for which the new data have fully established 16N as the series constant. The spectrum is similar to that of neutral sodium, Na I, but the main series which correspond with the familiar series of Na I are in the extreme ultra-violet, while the secondary series which partially fall within the ordinary range of observation correspond with series which occur in the infra-red in Na I.

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* E. Fues, 'Zeit. f. Phys.,' vol. 11, p. 365 (1922).

Including Paschen's recent work on Al III, and the author's previous work on Mg II, which also have spectra similar to that of Na I, data are thus available for the comparison of the spectra given by four similarly constituted atoms, which differ mainly in the charge of the nucleus. The doublet separations and the series terms show greater regularity than those for elements of the same chemical group.

The highest term of the Si IV system is 364117, corresponding to an ionisation potential of 44·95 volts.

The author desires to acknowledge his indebtedness to Messrs. J. S. Clark, J. A. Hey, H. Barrell and L. J. Freeman, who have at various times rendered valuable assistance in the laborious experimental work which forms the basis of the foregoing paper.

Vapour Pressure and Density of Sodium Chloride Solutions.

By W. R. Bousfield, K.C., F.R.S., and C. Elspeth Bousfield.

(Received March 7, 1923.)

Introduction.

The primary object of these experiments was to obtain a series of accurate determinations of the V.P. of aqueous NaCl solutions at 18° C., which might be used as a scale of reference for the determination of the V.P. of other salt solutions at the same temperature by the isopiestic method.

The ionisation laws of salt solutions sufficiently dilute are broadly known, but for more concentrated solutions the derivation of ionisation from conductivity data is complicated by changes in the composition of the water itself and in the amounts of water combined with and travelling with the ions. An attempt to resolve some of these difficulties was made in a former paper[*] by the use of V.P. data derived by extrapolation from Tamman's observations at temperatures from 40° C. to 100° C. Most of the reliable conductivity determinations are for a temperature of 18° C., and the process of extrapolation from the V.P. data at higher temperatures to 18° C. necessarily introduced inaccuracies. To carry the matter further more accurate determinations at 18° were necessary. By the method of isopiestic solutions[†] when an accurate scale of reference for one salt is obtained, it is easy to

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[*] Bousfield, 'Trans. Farad. Soc.,' vol. 15, p. 47 (1919).

[†] Bousfield, 'Trans. Farad. Soc.,' vol. 13, p. 401 (1918).

The Series Spectrum of Ionised Carbon (C II).

By A. Fowler, F.R.S., Yarrow Research Professor of the Royal Society,
Imperial College, South Kensington.

(Received February 15, 1924.)

Introductory.

For the development of the theory of atomic structure there would appear to be a special need for data relating to the series spectra of the lighter elements. It has, therefore, been thought desirable to publish the present account of the series of singly-ionised carbon without waiting for the completion of the investigation of the spectrum at other stages of ionisation.

It is an essential feature of Bohr's quantum theory of spectra that while the series constant for neutral atoms is nearly the same as that for hydrogen, the value of this constant will be increased four times when the atom is singly ionised, nine times when it is doubly ionised, 16 times when it is trebly ionised, and so on. Evidence that a system of series represents a particular stage of ionisation is thus to be sought in the value of the series constant for the system in question. Experimental confirmation has been obtained as far as the second ionisation by Paschen in the case of aluminium,* and as far as the third ionisation by the present writer in the case of silicon.†

The system of series dealt with in the present paper is characterised by a fourfold value of the hydrogen constant, and is accordingly attributed to singly-ionised carbon. The series may thus be designated C^+ or C II, those of the neutral atom being indicated by C or C I.

It may be remarked that the series of C I have not yet been identified. The only line which occurs in the arc spectrum in the ordinary region of observation is the well known line λ 2478, and observations in the extreme ultra-violet have hitherto only been made under conditions which generate the spectra of ionised atoms in addition to those of neutral atoms. The elimination of lines due to ionised atoms may perhaps simplify the identification of those belonging to the neutral atoms.

Experimental Procedure.

Extensive observations of the spectrum of carbon have been made over a wide range of wave lengths and under a variety of experimental conditions. The sources included the spark between graphite poles in air, the spark in hydrogen, the arc *in vacuo*, and carbon compounds—chiefly carbon-dioxide and hydrocarbons—in vacuum tubes. In connection with the vacuum tube observations the spectrum of oxygen under similar varied conditions was also investigated, so that the carbon lines could be distinguished in the mixed spectra of carbon and oxygen. The vacuum-tube spectra yielded lines of fine definition, which could be accurately measured in most cases. In the spark spectrum, the carbon lines are mostly diffuse, especially in the ultra-violet.

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* 'Ann. d. Phys.,' vol. 71, p. 142 (1923).

† 'Roy. Soc. Proc.,' A, vol. 103, p. 413 (1923).

Several of the lines in the ordinary region of observation which enter into the present discussion have been previously recorded, but few of them had been measured with sufficient accuracy for the present purpose. Among the newly-observed lines are a pair in the extreme red and three pairs in the ultra-violet.

Several spectrographs were utilised in the investigation, including a 10-foot concave grating, two large glass spectrographs, a quartz-Littrow spectrograph (Hilger's E 1), and a quartz spectrograph of ordinary construction (Hilger's E 2).

The standard lines adopted were those of iron, except in the region λ 2200 to λ 2100, for which Eder's wave-lengths of the copper spark lines* were used.

Several photographs have also been taken with a vacuum grating spectrograph. The carbon lines in the extreme ultra-violet, however, have already been measured by Simeon,† Millikan,‡ Hutchinson,§ and others. The wave-lengths and intensities given by these observers for lines which are believed to originate in C II are indicated in Table I.

The source employed by Simeon was the carbon arc in vacuo, while Millikan observed the spectrum of the "vacuum spark," and both sources were used by Hutchinson. There is a fairly close agreement between Simeon and Millikan, except for the last line, but the method of coincidences followed by Simeon is probably the most trustworthy, and Simeon's wave-lengths have accordingly been adopted. Evidence of their general accuracy is afforded by the close agreement of these wave-lengths with those calculated from the well-determined lines in the ordinary region of observation, as will appear from Table III. It may be noted that the pair of lines λ 1036 appeared in the second order on a plate of the carbon arc *in vacuo* taken in the course of the present investigation, and was very clearly resolved; the less refrangible component was decidedly

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[*] 'Zeit. f. Wiss. Phot.,' vol. 13, p. 24 (1914).

[†] 'Roy. Soc. Proc.,' A, vol. 102, p. 484 (1922), and vol. 104, p. 368 (1923).

[‡] 'Astrophys. Jour.,' vol. 53, p. 159 (1921).

[§] 'Astrophys. Jour.,' vol. 58, p. 291 (1923).

the brighter, as would be expected from the series discussion, though both were assigned intensity 5 by Simeon.

Table I.—Wave-lengths of C II Lines in Extreme Ultra-violet.

Simeon.		Millikan.		Hutchinson.		
	Intensity.		Intensity.		Intensity.	
					Arc.	Spark.
1036·84	5	1036·7	12	1037·2	10	8
1036·22	5					
858·2	7	858·5	5	858·9	8	7
687·1	7	687·3	8	687·1	6	8
636·2	2	636·3	3	636·8	—	2
594·9	4	595·1	5	595·5	1	5
560·5	2	560·5	2	562·0	—	1
543·4	1	543·5	1	544·0	—	0
533·9	1	533·3	1	—	—	—

Notation and Numeration.

The series rotation adopted is mainly that of the author's "Report on Series in Line Spectra."* Following the recent papers of Bohr and Paschen, however, the designation of the terms of the diffuse series has been changed, so that the terms $m\delta$, $m\delta'$ have become $m\delta_1$ and $m\delta_2$ respectively. This has the advantage of bringing the nomenclature of the diffuse terms into accordance with that for the terms of the principal series, lines involving π_1 or δ_1 being of greater intensity than those involving π_2 or δ_2. The use of Greek letters is merely to indicate that a system of doublets is under consideration.

The Rydberg and Ritz systems of numeration of the spectral terms have also been radically changed by Bohr on theoretical grounds, and in view of their possible permanence the new numbers have been introduced into the tables which follow. The numbers on the Rydberg system, however, are also given (in brackets) to facilitate comparison with earlier tables of series. It may be remarked that the empirical formulæ of Rydberg, Ritz and Hicks give no direct indication of Bohr's numbers, although they can be adapted to include them. On the new system, groups of electrons in the normal atom, such as were formerly supposed to be arranged in rings about the nucleus, are characterised by successive principal quantum numbers increasing outwards, and the four outer electrons in the carbon atom (atomic No. = 6) are accordingly assigned the quantum number 2. The subsidiary, or azimuthal, quantum number, however, is not necessarily or usually the same for all the electrons of a group.

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* Physical Society, London, p. 18 (1922).

Identification of the Series.

From the beginning of the investigation it seemed probable that the well-known pair of spark lines in the red, near λ 6580, must belong to a principal series. Existing data* suggested that pairs of lines about λ 2837 and λ 3920 might have the same separation and be associated with the red pair. The experimental work confirmed this equality of separation and revealed similarly related pairs about λ 2747 and λ 2402. With these data, omitting the pair at λ 2837 and assuming the series constant to be 4N, the main features of the series were suggested, and the approximate positions of other lines were calculated. Special search for these lines was instituted, and some of them were identified, notably a pair in the extreme red about λ 7236 and a second member of the principal series at λ 2174. The identification of this red pair led in turn to the recognition of the fundamental series, the first member of which is the well-known spark line at λ 4267. Much embarrassment was caused throughout by the strong pair at λ 2837, which apparently had no place in the series thus suggested.

It was clear that associated stronger series might be expected in the extreme ultra-violet. An approximate limit for the subordinate series, 2 (1) π, could be calculated from the two π terms already obtained, and thence the approximate positions of lines by the use of the already known terms. The identifications, however, were actually made by sorting out wave-numbers which differed by the same amounts as the known terms, assuming that the tabulated lines were unresolved doublets. Next, with a Hicks formula, the three lines λλ 594·9, 560·5 and 543·4, with 4N for series constant, led to the limit 2 (1) $\pi_1 = 196643$, but this might have been considerably in error because of the great influence of small errors of wave-length on the wave-numbers. A more exact value of the limit was obtained through the outstanding pair at λ 2837 and the strong pair at λ 1036 by introducing a term x as shown under "combinations" at the foot of Table III. In this way, the separation ($\Delta\nu = 58$) of the pairs of the series in the extreme ultra-violet was deduced.

The significance of the x term is not clear. It is probable, however, that it is of the σ type, because it gives the normal separation to the pair at λ 2837 and

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* Kayser's 'Handbuch,' vol. 5, p. 225.

Table II.—List of C II Lines.

λ, I.A.	Intensity.	ν.	Series.	Remarks.
† 7236·19	8*n*	13815·63	$3(2)\pi_1-3(2)\delta_1$	Grating, 5·5 A per mm.
7231·12	6*n*	13825·31	$3(2)\pi_2-3(2)\delta_2$	
6582·85	8	15186·80	$3(2)\sigma-3(2)\pi_2$	Grating, 5·5 A per mm.
6578·03	10	15197·93	$3(2)\sigma-3(2)\pi_1$	
5891·65	2	16968·48	$4(3)\pi_2-4(2)\delta_2$	Glass sp., 10 A per mm.
5889·97	3	16973·32	$4(3)\pi_1-4(2)\delta_1$	
‡ 4267·27	10*n*	23427·61	$3(2)\delta_1-4(3)\phi$	Glass sp., 2·6 A per mm.
4267·02	8*n*	23428·99	$3(2)\delta_2-4(3)\phi$	
3920·773	8	25497·98	$3(2)\pi_1-4(3)\sigma$	Glass sp., No. 2, 4·6 A per mm.
3919·061	6	25509·11	$3(2)\pi_2-4(3)\sigma$	
2992·63	4*n*	33405·71	$3(2)\ \delta-5(4)\phi$	Quartz sp. E 1, 4·6 A per mm.
2837·602	8	35230·69	$x\ -3(2)\pi_2$	Grating, 2·8 A per mm.
2836·710	10	35241·75	$x\ -3(2)\pi_1$	
¶ 2747·31	6*n*	36388·52	$3(2)\pi_1-4(3)\delta_1\delta_2$	Quartz spec. E 1, 3·7A per mm.
2746·50	4*n*	36399·24	$3(2)\pi_2-4(3)\delta_2$	
§ 2574·86	1*n*	38825·45	$3(2)\delta-6(5)\phi$	Quartz spec. E 1, 3·1A per mm.
* 2402·40	2*n*	41612·37	$3(2)\pi_1-5(4)\sigma$	Quartz spec. E 1, 2·4 A per mm.
2401·77	1*n*	41623·27	$3(2)\pi_2-5(4)\sigma$	
† 2174·14	1	45980·82	$3(2)\sigma-4(3)\pi_2$	Quartz spec. E 2, 5·5 A per mm.
2173·86	2	45986·74	$3(2)\sigma-4(3)\pi_1$	
† 2137·93	1*n*	46759·34	$3(2)\pi_1-5(4)\delta_1\delta_2$	Quartz spec. E 2, 5·3 A per mm.
2137·45	1*n*	46769·84	$3(2)\pi_2-5(4)\delta_2$	
‖ 1036·84	5	96447	$2(1)\pi_1-x$	Vacuum sp. (Simeon).
1036·22	5	96505	$2(1)\pi_2-x$	
858·2	7	116523	$2(1)\pi-3(2)\sigma$	Vacuum sp. (Simeon), Unresolved pair.
687·1	7	145539	$2(1)\pi-3(2)\delta$	Vacuum sp. (Simeon), Unresolved pair.
636·2	2	157183	$2(1)\pi-4(3)\sigma$	Vacuum sp. (Simeon), Unresolved pair.
594·9	4	168095	$2(1)\pi-5(4)\delta$	Vacuum sp. (Simeon), Unresolved pair.
560·5	2	178412	$2(1)\pi-5(4)\delta$	Vacuum sp. (Simeon), Unresolved pair.
543·4	1	184026	$2(1)\pi-6(5)\delta$	Vacuum sp. (Simeon), Unresolved pair.
533·9	1	187301	$2(1)\pi-7(6)\delta$	Vacuum sp. (Simeon), Unresolved pair.

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* Eder & Valenta, 2402·1 (1*n*).

† Not previously recorded.

‡ First resolved by A. S. King ('Astrophys. Jour.,' vol. 38, p. 329 (1913).

§ Eder & Valenta, 2576·7 (1).

‖ The less refrangible line is the stronger.

¶ Eder & Valenta, 2747·3 (3).

leads to no fundamental series if supposed to be of δ type. There is a somewhat similar term in the series of Si II, as will be shown in a subsequent paper, but in that case it is certainly of δ type.

The lines which are considered to be definitely included in the series system of ionised carbon are brought together in the order of wave-lengths in Table II, which is self-explanatory. Wave-lengths from 1036 A downwards are the values *in vacuo* according to the measurements of Simeon. Particulars as to the instruments used for the determination of individual wave-lengths are given in the last column of the table, which also indicates the dispersion in Angstroms per millimetre at the respective wave-lengths. On account of the diffuse character of some of the lines, the accuracy of the wave-lengths is probably not in every case commensurate with the dispersion employed, but the errors are not likely to exceed a few hundredths of an Angstrom.

Several lines which occur in the carbon spark are not included in the above list and may possibly belong to series representing higher degrees of ionisation. Many lines which do not appear in the spark have, in fact, been obtained by passing strong discharges through carbon compounds in vacuum tubes.

The Series Limits.

Justification for the adoption of 4N as the series constant for the spectrum under consideration is found in the consistency of the various terms when this assumption is made in the calculation of limits. With the exception of the first diffuse series, there is unfortunately no observed series which is long enough to permit the use of a four-constant formula. This series is not very suitable for the independent calculation of the series constant, partly because diffuse series are often imperfectly represented by formulæ, and partly because of the possible large errors in the wave-numbers, but the following formula may be quoted as representing the first four members :—

$$\nu = 197003 - 487868 \Big/ \left(m + 1 \cdot 166484 - \frac{0 \cdot 175114}{m}\right)^2 .$$

The value of the constant thus calculated is 4·45N, which is, perhaps, as near to 4N as is to be expected from the nature of the data. As indicating the uncertainty in the calculation of the constant from this series it may be noted that a decrease of only one-tenth of an Angstrom in the wave-length of the line λ 560·5 leads to the value 436018 or 3·975N, and the limit 196500.

More exact values of the limits and spectral terms may be derived from the measurements in the ordinary region of the spectrum, for which greater dispersion could be utilised. Formulæ were accordingly calculated as follows :—

2nd Sharp Series. $3(2)\pi_1 - m\sigma$.

$$\begin{array}{r} -15197\cdot93\\ 25497\cdot98\\ 41612\cdot37\end{array}\left\{\begin{array}{l}\nu = 65045\cdot37 + 4\mathrm{N}\Big/\left(m + 0\cdot315569 + \dfrac{0\cdot045305}{m}\right)^2\\ \qquad 3(2)\,\pi_1 = 65045\cdot37\\ \qquad 3(2)\,\pi_2 = 65056\cdot50\end{array}\right.$$

2nd Diffuse Series. $3(2)\,\pi_2 - m\delta_2$.

$$\begin{array}{r} 13825\cdot31\\ 36399\cdot24\\ 46769\cdot84\end{array}\left\{\begin{array}{l}\nu = 64888\cdot50 + 4\mathrm{N}\Big/\left(m + 0\cdot910270 + \dfrac{0\cdot041740}{m}\right)^2\\ \qquad 3(2)\,\pi_1 = 64877\cdot37\\ \qquad 3(2)\,\pi_2 = 64888\cdot50\end{array}\right.$$

Fundamental Series. $3(2)\,\delta_1 - m\phi$.

$$\begin{array}{r} 23427\cdot61\\ 33405\cdot71\\ 38825\cdot45\end{array}\left\{\begin{array}{l}\nu = 51107\cdot56 + 4\mathrm{N}\Big/\left(m + 0\cdot969722 + \dfrac{0\cdot034111}{m}\right)^2\\ \qquad 3(2)\,\pi_1 - 3(2)\,\delta_1 = 13815\cdot63\\ \qquad\qquad 3(2)\,\pi_1 = 64923\cdot19\\ \qquad\qquad 3(2)\,\pi_2 = 64934\cdot32\end{array}\right.$$

The mean of the three values for $3(2)\pi_1$ is 64948, but since the negative wave-number in the 2nd sharp series is unfavourable to a good determination of the limit, and diffuse series are usually not well represented by the empirical formulæ, it has been considered best to adopt the values determined from the fundamental series, namely,

$$3(2)\,\pi_1 = 64923\cdot19$$
$$3(2)\,\pi_2 = 64934\cdot32$$

The limits of the other series then follow when the corresponding terms and lines are combined in the usual manner. The decimal parts have, of course, no claim to significance, and are only retained to preserve accuracy in the combination of terms.

The Series System of C II.

Details as to the various series of C II which have so far been traced are given in Table III, which is arranged on the plan adopted in the author's "Report on Series," and calls for little further explanation. It is only necessary to note that the lines of the first sharp and first diffuse series have not been resolved, and that their separations have been assumed to be the same as the separation of the pair at λ 1036, as measured by Simeon. Assuming the latter to have been accurately measured, the positions of the other members in the region of short

Table III.—Series of C II.

1st Sharp Series. $2(1)\pi - m\sigma$.

$2(1)\pi_1 = 196612$; $2(1)\pi_2 = 196670$.

Observed.		Calculated.		Δν.	m	mσ.
λ, Intensity.	ν.	λ.	ν.			
					B. R.	
858·2 (7)	116523	858·43 858·00	116491 116549	[58]	3 (2)	80121
636·2 (2)	175183	636·18 635·95	157187 157245	,,	4 (3)	39425
—	—	577·03 576·83	173301 173359	,,	5 (4)	23311
—	—	551·80 551·63	181225 181283	,,	6 (5)	[15387]

1st Diffuse Series. $2(1)\pi - m\delta$.

$2(1)\pi_1 = 196612$; $2(1)\pi_2 = 196670$.

Observed.		Calculated.		Δν.	m.	mδ.
λ, Intensity.	ν.	λ.	ν.			
					B. R.	
687·1 (7)	145539	687·27 686·99	145504 145562	[58]	3 (2)	51108
594·9 (4)	168095	594·96 594·76	168077 168135	,,	4 (3)	28535
560·5 (2)	178412	560·39 560·21	178448 178506	,,	5 (4)	18164
543·4 (1)	184026	543·32 543·15	184054 184112	,,	6 (5)	[12558]
533·9 (1)	187301	533·56 533·40	187419 187477	,,	7 (6)	[9193]

Fundamental Series. $3(2)\delta - m\phi$.

$3(2)\delta_1 = 51107{\cdot}56$; $3(2)\delta_2 = 51108{\cdot}94$.

λ, Intensity.	ν.	Δν.	m	mφ.	Remarks.
			B. R.		
4267·27 (10) 4267·02 (8)	23427·61 23428·99	1·38	4 (3)	27679·95	
2992·63 (4*n*)	33405·71	—	5 (4)	17702·54	Mean $\delta_1\delta_2$ taken.
2574·86 (1*n*)	38825·45	—	6 (5)	12282·80	Mean $\delta_1\delta_2$ taken.
[2375·1]	[42091]	—	—	[9017·0]	

Principal Series. 3 (2) σ − mπ.
3 (2) σ = 80121·12.

λ, Intensity.	ν.	Δν.	m.	mπ₁, mπ₂.
			B. R.	
6578·03 (10) 6582·85 (8)	15197·93 15186·80	11·13	3 (2)	64923·19 64934·32
2173·86 (2) 2174·14 (1)	45986·74 45980·82	5·92	4 (3)	34134·38 34140·30

2nd Sharp Series. 3 (2) π − mσ.
3 (2)π_1 = 64923·19 ; 3 (2) π_2 = 64934·32.

λ, Intensity.	ν.	Δν.	m.	mσ.
			B. R.	
−6578·03 (10) −6582·85 (8)	−15197·93 −15186·80	11·13	3 (2)	80121·12
3920·773 (8) 3919·061 (6)	25497·98 25509·11	11·13	4 (3)	39425·21
2402·40 (2n) 2401·77 (1n)	41612·37 41623·27	10·90	5 (4)	23310·82
[2018·1] [2017·6]	[49536] [49547]		6 (5)	[15387]

2nd Diffuse Series. 3 (2) π − mδ.
3 (2) π_1 = 64923·19 ; 3 (2) π_2 = 64934·32.

λ, Intensity.	ν.	Δν.	m.	$m\delta_2$, $m\delta_1$. ($m\delta'$, $m\delta$.)
			B. R.	
§ — 7236·19 (8n) 7231·12 (6n)	[13814·18] 13815·63 13825·31	[1·45] [11·13]	3 (2)	51109·01 51107·56
§ — 2747·31 (6r) 2746·50 (5r)	[36388·11] 36388·52 36399·24	[0·41] [11·13]	4 (3)	28535·08 28534·67
2137·93 (1n) 2137·45 (1n)	46759·34 46769·84		5 (4)	18164·2
			6 (5)	[12558]
			7 (6)	[9193]

3rd Diffuse Series. 4 (3) π − mδ.
4 (3) π_1 = 34134·38 ; 4 (3) π_2 = 34140·30.

λ, Intensity.	ν.	Δν.	m.	$m\delta_2$, $m\delta_1$.
§ — −5889·97 (3) −5891·65 (2)	— −16973·32 −16968·48		3 (2)	51108·78 51107·70

Combinations.

λ, Intensity.	ν.	Δν.
−2836·710 (10) −2837·602 (8)	−35241·75 −35230·69	11·06
1036·84 (5) 1036·22 (5)	96447 96505	58

Derivation of x, 2 (1) π_1 and 2 (1) π_2.

$$\left.\begin{array}{l} 3\,(2)\,\pi_1 - x \\ 3\,(2)\,\pi_2 - x \end{array}\right\} \quad x = 100164{\cdot}9.$$

$$\left.\begin{array}{l} 2\,(1)\,\pi_1 - x \\ 2\,(1)\,\pi_2 - x \end{array}\right\} \quad \begin{array}{l} 2(1)\,\pi_1 = 196612. \\ 2(1)\,\pi_2 = 196670. \end{array}$$

§ Satellites not directly observed.

n = Diffuse.

r = Diffuse to red.

wave-lengths have been calculated, and it will be seen that there is a very satisfactory agreement with the observed values. The greatest divergence is in the line λ 533·9 for which, however, the mean of Simeon's and Millikan's values is in close agreement with the calculated position.

The Series Terms.

The series terms may be conveniently summarised as in Table IV. A few additional terms have been extrapolated from the known terms by formulæ calculated from the last two observed values in each series. Thus—

$$\left.\begin{matrix}39425\cdot2\\23310\cdot8\end{matrix}\right\} \quad m\sigma = 4\mathrm{N}\Big/\left(m+0\cdot345406-\frac{0\cdot028740}{m}\right)^2$$

$$\left.\begin{matrix}28534\cdot7\\18164\cdot2\end{matrix}\right\} \quad m\delta_1 = 4\mathrm{N}\Big/\left(m+0\cdot894946+\frac{0\cdot078348}{m}\right)^2$$

$$\left.\begin{matrix}17702\cdot5\\12282\cdot8\end{matrix}\right\} \quad m\phi = 4\mathrm{N}\Big/\left(m+0\cdot969307+\frac{0\cdot035580}{m}\right)^2$$

Calculated terms are shown in brackets.

Table IV.—Series Terms of C II.

Bohr's numbers.	2	3	4	5	6	7
mx	—	100165				
$m\sigma$	—	80121	39425	23311	(15387)	(10912)
$m\pi_2$	196670	64934	34140			
$m\pi_1$	196612	64923	34134			
$m\delta_2$	—	51108·9	28535·1	18164	(12558)	(9193)
$m\delta_1$	—	51107·6	28534·7			
$m\phi$	—	—	27680	17703	12283	(9017)
$4\mathrm{N}/m^2$	(109678)	(48746)	(27420)	(17549)	(12187)	(8953)

The corresponding "effective quantum numbers" are given in Table V, these being the values of the square root of 4N/T, where T is the term.

Table V.—Effective Quantum Numbers.

Bohr's numbers.	2	3	4	5	6	7
mx	—	2·092822				
$m\sigma$	—	2·340005	3·335826	4·338221	5·339658	6·340616
$m\pi_2$	1·493555	2·599281	3·584732			
$m\pi_1$	1·493775	2·599504	3·585043			
$m\delta_2$	—	2·929826	3·921036	4·914533	5·910616	6·908004
$m\delta_1$	—	2·929865	3·921062			
$m\phi$	—	—	3·981142	4·978202	5·976423	6·974237

It will be observed that the decimal parts of the numbers for the σ terms decrease from the first to the second, and afterwards increase, and that the π terms first show an increase and then a decrease. This is unusual, but occasionally occurs in connection with δ terms in other spectra.

Conclusions.

From the foregoing observations and calculations it is clear that the spectrum of ionised carbon consists of a doublet system, as would be expected from the spectroscopic displacement law. The spectrum would, in fact, be expected to be of the same type as that of the neutral atoms of boron, the element which precedes carbon in the periodic system. The series system of neutral boron has not yet been traced, but there is evidence to show that it consists of doublets,* like the spectra of other elements of the third group. The arrangement of the electronic orbits in neutral boron is not certainly known, but Bohr† has supposed that two of the three outer electrons are in 2_1 orbits and the third probably in a 2_2 orbit. The last named would be more loosely bound than the others, and the largest series term would accordingly be a p term corresponding with the subordinate (or azimuthal) quantum number 2. This view of the structure of the boron atom is in accordance with the series data for C II, from which it will be seen that the largest known term is 2π; the electron which produces the spectrum must therefore occupy a 2_2 orbit in the normal state of the ionised atom.

The value 196670 for the highest series limit of C II corresponds to a second ionisation potential of 24·28 volts, representing the energy necessary to remove the second electron when the first has already been removed. The first ionisation potential is not known, as the series of C I have not yet been worked out, but Saunders* has suggested that it may be from 7 to 8 volts.

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* 'Report on Series,' p. 155.

† 'Ann. d. Phys.,' vol. 71, p. 260 (1913).

Summary.

The production of previously unrecorded lines of carbon has led to the identification of the leading members of the series of ionised carbon (C II or C^+) in the ordinary region of observation. The main series, however, lie in the extreme ultra-violet and were identified in the observations of Simeon and Millikan with the aid of the spectral terms thus determined. The series of C II form a doublet system, like the spectra of boron and other elements of Group III, as would be expected from the spectroscopic displacement law. The highest terms are the common limits of the sharp and diffuse series, 196612 and 196670, from which it may be deduced that the second ionisation potential of carbon is 24·3 volts.

In the normal state of the atoms, two of the outermost electrons in ionised carbon probably move in 2_1 orbits, while the electron which generates the spectrum traverses a 2_2 orbit, as suggested by Bohr for neutral boron.

The author has pleasure in acknowledging the valuable assistance in the experimental work which has been given at different times by Mr. J. Brooksbank, Miss Saltmarsh, and Mr. E. W. H. Selwyn.

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* 'Science,' No. 1516, Jan., 1924.

The Structure of the Spectrum of Ionised Nitrogen.

By A. Fowler, F.R.S., Yarrow Research Professor of the Royal Society,
Imperial College, South Kensington.

(Received November 10, 1924.)

[Plate 1.]

Introductory.

In accordance with recent developments in the analysis of spectra, it is to be expected that, while the neutral atom of nitrogen (N I) will yield a spectrum derived from systems of terms of even multiplicity, the spectrum of ionised nitrogen (N II or N^+) will be constituted from terms of odd multiplicity. The spectrum of doubly-ionised nitrogen (N III or N^{++}) is similarly expected to be formed from terms of even multiplicity.

The probable existence of the three types of line spectra representing N I, N II and N III has already been pointed out,* but few details regarding the regularities in the respective spectra have hitherto been available. A spectrum which probably represents N I has been described by Stark and Hardtke,† but accurate measurements of the lines do not appear to have been made; Bowen and Millikan,‡ however, have attributed to N I two well-known pairs of lines in the Schumann region at λλ 1745·3, 1742·7, 1494·8 and 1492·8, implying even multiplicity of the terms involved.

While the present paper has been in preparation, Ruark and his colleagues§ have recognised one of the main groups of N II lines as a multiplet of the type known as $mp - np'$, or pp', and have indicated two pairs of lines having the separation $\Delta\nu = 51 \cdot 69$. Several lines in the extreme red have further been attributed to N II by Kiess,|| and have been classified as resulting from combinations of a triple p term with an s term, another triple p term, and with a five-fold d term, all of which belong to quintet systems. None of these quintet terms have yet been found to be involved in the structure of the spectrum from λ 6650 to λ 2200 which is discussed in the present paper; all the terms

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* Fowler's 'Report on Series,' p. 165 (1922).

† 'Ann. d. Phys.,' vol. 56, p. 363 (1918).

‡ 'Physical Review,' vol. 24, p. 214 (1924).

§ 'Sci. Pap. Bur. Stand., Washington,' No. 490 (1924).

|| 'Science,' vol. 60, p. 249 (Sept., 1924).

so far discovered from groups of lines in this region belong to systems of singlets and triplets.

The third spectrum is still under investigation, but there is no doubt that it includes a doublet system similar to those of elements of the third group.

The present communication gives particulars of the regularities which have been recognised in the second line spectrum of nitrogen. It is not yet possible to give the absolute values of the terms, but the relative values can be stated with considerable accuracy.

Observational Data.

The second line spectrum of nitrogen is well known from its occurrence, in company with lines of oxygen, in the spectrum of air which appears in the ordinary spark spectra of metals. For the present purpose, however, extensive observations have also been made of the spectrum of nitrogen in vacuum tubes, with the gas at various pressures and under varying conditions of electrical discharge. In this way it has been possible to separate the different classes of lines and to obtain most of the lines with sufficient sharpness to permit accurate determinations of wave-lengths. A few lines which are of importance for the analysis of the spectrum do not appear to have been previously recorded. The spectrum has been investigated over the range λ 6650 to λ 2200, but no regularities have yet been traced on the more refrangible side of λ 3000.

All the lines between λ6650 and λ3000 which have been classified are collected in Table I. The wave-lengths are on the international scale, and most of them have been obtained with adequate dispersion and resolving power. Numbers in brackets following the wave-lengths indicate intensities, and the wave-numbers have been corrected to vacuum in the usual way. Term combinations are shown in the final column.

Triplets and Multiplets.

The analysis of a spectrum of the kind under consideration is greatly facilitated by the assignment of a value to one of the terms, even if it be entirely arbitrary. A rough approximation to the largest term of N II, however, may be obtained from astrophysical data. In a discussion of the spectra of stars from the point of view of the stages at which typical lines attain their maximum intensity, in conjunction with ionisation potentials already determined from the series of carbon, silicon and other elements, Miss C. H. Payne* has estimated the ionisation potential of N II as 24 volts. A similar value has

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* 'Harvard Coll. Obs. Circular,' No. 256 (1924).

Table I.—Classified Lines of N II.

λ, I.A. (inty.).	ν.	Combinations.
5961·25 (0)	16770·36	$p'_1 - d'_3$
5952·57 (3)	16794·81	$p'_1 - d'_2$
5941·90 (8)	16824·99	$p'_1 - d'_1$
5940·42 (2)	16829·18	$p'_2 - d'_3$
5931·96 (7)	16853·18	$p'_2 - d'_2$
5928·02 (4)	16864·37	$p'_3 - d'_3$
5767·47 (2)	17333·83	$P - d_3$
5747·32 (3)	17394·60	$P - d_2$
5730·64 (0)	17445·23	$p_1 - d_3$
5710·64 (5)	17506·33	$p_1 - d_2$
5686·20 (6)	17581·57	$p_2 - d_3$
5679·49 (10)	17602·33	$p_1 - d_1$
5675·96 (6)	17613·30	$p_3 - d_3$
5666·54 (8)	17642·57	$p_2 - d_2$
5495·89 (4)	18190·38	$\Delta\nu = \Delta p^2_{23}$
5480·29 (1)	18242·15	
5073·55 (1)	19704·59	$P - s$
5045·02 (5)	19816·03	$p_1 - s$
5010·54 (4)	19952·39	$p_2 - s$
5002·66 (2)	19983·81	$p_3 - s$
4810·27 (2)	20783·07	$d_1 - d'_2$
4803·30 (6)	20813·22	$d_1 - d'_1$
4793·66 (2)	20855·06	$d_2 - d'_3$
4788·13 (5)	20879·18	$d_2 - d'_2$
4781·21 (2)	20909·44	$d_2 - d'_1$
4779·72 (4)	20915·91	$d_3 - d'_3$
4774·24 (2)	20939·91	$d_3 - d'_2$
4674·98 (2)	21384·50	$P - p'_3$
4667·28 (2)	21419·78	$P - p'_2$
4654·57 (2)	21478·27	$P - p'_1$

λ, I.A. (inty.).	ν.	Combinations.
*4643·106 (8)	21531·30	$p_1 - p'_2$
4630·551 (10)	21589·67	$p_1 - p'_1$
4621·405 (7)	21632·41	$p_2 - p'_3$
4613·884 (6)	21667·66	$p_2 - p'_2$
4607·167 (7)	21699·26	$p_3 - p'_2$
4601·490 (8)	21726·03	$p_2 - p'_1$
4236·99 (6*n*)	23595·04	$\Delta\nu = \Delta p^2_{23}$
4227·738 (3*n*)	23646·68	
4043·54 (2*n*)	24723·84	$\Delta\nu = \Delta p^2_{23}$
4035·090 (3*n*)	24775·62	
3994·995 (10)	25024·27	$P - S$
3955·851 (5)	25271·88	$p_2 - S$
3856·07 (3)	25925·81	$p'_1 - p^2_2$
3855·08 (3)	25932·48	$p'_2 - p^2_3$
3847·38 (2)	25984·37	$p'_2 - p^2_2$
3842·20 (2)	26019·40	$p'_3 - p^2_2$
3838·39 (4)	26045·23	$p'_1 - p^2_1$
3829·80 (3)	26103·65	$p'_2 - p^2_1$
3615·88 (1)	27647·94	$s - p^2_3$
3609·09 (2)	27699·93	$s - p^2_2$
3593·60 (3)	27819·34	$s - p^2_1$
3437·162 (6)	29085·46	$P - S^2$
3408·136 (3)	29333·17	$p_2 - S^2$
3331·32 (3)	30009·52	$d_2 - p^2_2$
3330·30 (2)	30018·70	$d_3 - p^2_3$
3328·79 (4)	30032·34	$d_1 - p^2_1$
3324·58 (2)	30070·37	$d_3 - p^2_2$
3318·14 (2)	30128·72	$d_2 - p^2_1$
	†30189·69	$d_3 - p^2_1$
3006·86 (7)	33247·67	P – D (?)

* The wave-lengths from λ 4643 to λ 4035, with the exception of λ 4043·54, were determined by J. S. Clark ('Astrophys. Jour.,' vol. 40, p. 333 (1914)).

† Calculated wave-number.

been deduced by R. H. Fowler and E. A. Milne.* The present investigation indicates that the highest term is a *p* term, and adopting the usual relation,† the corresponding value of the term 1*p* is 194,000. The related term, 2*p*, which is applicable to the region here considered would accordingly have a value of the order of 70,000, it being assumed that the series constant is 4R (R = 109678·3). The non-appearance of certain groups which might be expected to fall within the range of spectrum observed suggests that this value for $2p$ may be too low, but it will at least serve the same purpose as a value chosen at random. It is to be understood that while the values assigned to the respective terms may be considerably in error, the differences of term values are correct within the limits of error of the observations.

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* 'Mon. Not. R.A.S.,' vol. 84, p. 506 (1924).

† Fowler's 'Report,' p. 69.

For the schematic representation of the structure of the triplets and multiplets, it will suffice to quote the wave-numbers of the lines; the corresponding wave-lengths may be found by reference to Table I. Numbers in brackets following the wave-numbers indicate intensities, and differences of terms are printed in italics.

The assignment of inner quantum numbers (j) is in accordance with the work of Sommerfeld and Landé,* and has led to the identification of the types of terms involved in the various groups of lines. The selection rule in relation to these inner quantum numbers, it may be mentioned, is that $\Delta j = \pm 1$ or 0, with the exception that the transition 0 to 0 does not ordinarily occur. It may eventually be found convenient to adopt the inner quantum numbers as suffixes in place of those in common use for the designation of members of multiple terms, but, for the present, it has been thought desirable to continue the use of the older nomenclature and to give the values of j separately.

For the sake of brevity, combinations such as $mp - np'$ are contracted to pp', since sequences of terms have not yet clearly entered into the discussion.

One of the most striking groups of lines of N II is that about λ 4630 (No. 3, Plate 1), and it will be convenient to consider this first, because it has been very accurately measured by Clark and fixes the triplet character of some of the terms. The structure of the group may be shown as follows :—

p'_3		p'_2		p'_1		
(0)		(1)		(2)		j
		21531·30(8)	*58·37*	21589·67(10)	p_1	(2)
		136·36		*136·36*		
21632·41(7)	*35·25*	21667·66(6)	*58.37*	21726·03(8)	p_2	(1)
		31·60				
		21699·26(7)			p_3	(0)

$p_1 = 70000 \cdot 00$† ; $p_2 = 70136 \cdot 36$; $p_3 = 70167 \cdot 96$

$p'_1 = 48410 \cdot 33$; $p'_2 = 48468 \cdot 70$; $p'_3 = 48503 \cdot 95$

This group is clearly of the pp' type, consisting of six lines, and the inner quantum numbers adapted to the group indicate that each set of terms belongs to a triplet system. If the p and p' terms belonged to quintet systems, all the values of j would be increased by unity and a seventh line, $p_3p'_3$, would be expected. The p terms involved in the above combinations are doubtless equivalent to the $2p$ terms of ordinary series, since the series constant must be 4R; the $1p$ term must be much greater. The interval rule of Landé gives a ratio of 2 : 1 for the separations of triplet p terms, and it will be observed that this is far from being followed in N II; the rule probably also ceases to be applicable to other elements in the first row of the periodic table.

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* 'Zeit. f. Phys.,' vol. 15, p. 191 (1923).

† Assumed value.

Attention may next be directed to a complex diffuse triplet which includes the strong lines in the yellow-green about λ 5680 (Nos. 1 and 2, Plate 1). This may be represented as follows:—

d_3		d_2		d_1		
(1)		(2)		(3)		j
17445·23(0)	*61·10*	17506·33(6)	*96·00*	17602·33(10)	p_1	(2)
136·34		*136·24*				
17581·57(5)	*61·00*	17642·57(8)			p_2	(1)
31·73						
17613·30(6)					p_3	(0)

$$d_1 = 52397{\cdot}67\,;\ d_2 = 52493{\cdot}73\,;\ d_3 = 52554{\cdot}74$$

The triplet character of the d terms is thus fully established by the values which have to be assigned to j in order to conform with the inner quantum selection rule. The appearance of this diffuse triplet differs very considerably from that of the more familiar triplets which occur in the spectra of elements of the second group, as will be seen from fig. 1.

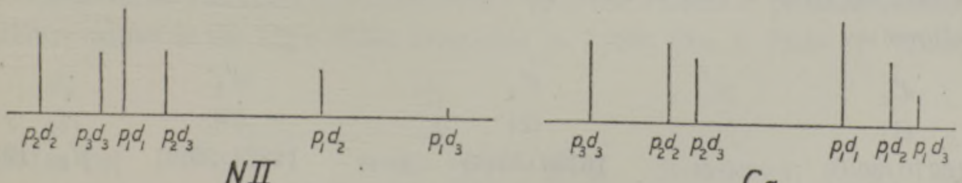

FIG. 1.—The diffuse triplet of N II near λ 5680, compared with a diffuse triplet of calcium.

The apparent distortion obviously arises from the fact that in the N II group the differences between the d terms are much larger in comparison with those of the p terms than in the diffuse triplets of calcium and other elements of the second group.

The separations Δp_{12} and Δp_{23} occur also in connection with three lines forming part of the well-known cluster of lines about λ 5007. The wave-numbers are :—

p_1 (2)		p_2 (1)		p_3 (0)		j
19816·03(5)	*136·36*	19952·39(4)	*31·42*	19983·81(2)	s	(1)

$s = 50184·30$

The associated term must clearly have $j = 1$, and may accordingly be a singlet P term, or an s term of a triplet system. The restrictions as to azimuthal quantum numbers, however, would ordinarily exclude P, and the term is therefore probably of the s type.

A multiplet of the triplet dd' type may be next conveniently considered. This is of "skew-symmetrical" structure, consisting of three strong and four weaker lines, and is shown as No. 3, Plate 1. The structure may be shown as below :—

d'_3 (1)		d'_2 (2)		d'_1 (3)		j
		20783·07(2)	*30·15*	20813·22(6)	d_1	(3)
		96·11		*96·22*		
20855·06(2)	*24·12*	20879·18(5)	*30·26*	20909·44(2)	d_2	(2)
60·85		*60·73*				
20915·91(4)	*24·00*	20939·91(2)			d_3	(1)

$d'_1 = 31584·37$; $d'_2 = 31614·66$; $d'_3 = 31638·75$.

The new d' terms thus introduced reappear in a $p'd'$ combination which forms a very characteristic group of lines in the orange, the brightest line being λ 5941·90 (Nos. 1 and 2, Plate 1). The wave-numbers may be arranged as follows :—

d'_3 (1)		d'_2 (2)		d'_1 (3)		j
16770·36(0)	*24·45*	16794·81(3)	*30·18*	16824·99(8)	p'_1	(2)
58·82		*58·37*				
16829·18(2)	*24·00*	16853·18(7)			p'_2	(1)
35·19						
16864·37(4)					p'_3	(0)

Like the pd group previously described, this group differs considerably in appearance from the more familiar diffuse triplets in the spectra of elements of the second group.

A further set of triplet terms of p type, designated p^2 for reasons given later, appears in a multiplet having its brightest member at λ 3838 (No. 4, Plate 1). The new terms combine with the previously determined p' terms as shown below :—

p^2_3		p^2_2		p^2_1		
(0)		(1)		(2)		j
		25925·81(1)	*119·42*	26045·23(3)	p'_1	(2)
		53·56		*58·42*		
25932·48(2)	*51·89*	25984·37(1)	*119·28*	26103·65(3)	p'_2	(1)
		35·03				
		26019·40(1)			p'_3	(0)

$$p^2_1 = 22365\cdot05 \; ; \; p^2_2 = 22484\cdot47 \; ; \; p^2_3 = 22536\cdot22.$$

The lines of this group are remarkable for the fact that all of them were broadened and displaced towards the red by about 0·7A in a tube containing nitrogen at relatively high pressure. The wave-numbers quoted are from measurements on tubes at low pressures, where the lines were sharply defined.

The same phenomenon of a large displacement towards the red was observed in connection with an isolated triplet in the ultra-violet (Nos. 4 and 5, Plate 1), in which the characteristic separations of the p^2 terms also appear ; the wave-numbers are as follows :—

p^2_3		p^2_2		p^2_1		
(0)		(1)		(2)		j
27647·94(1)	*51·99*	27699·93(2)	*119·41*	27819·34(3)	s	(1)

The singlet term entering into this combination is the s term already deduced from sp.

The p^2 terms also enter into combination with the d terms to produce another diffuse triplet in the ultra-violet, beginning at λ 3331 (No. 5, Plate 1). Thus,

d_3		d_2		d_1		
(1)		(2)		(3)		j
[30189·69]	*60·97*	30128·72(2)	*96·38*	30032·34(4)	p^2_1	(2)
119·32		*119·20*				
30070·37(2)	*60·85*	30009·52(3)			p^2_2	(1)
51·66						
30018·71(2)					p^2_3	(0)

The line for which the calculated position is ν 30189 would be expected to be faint, and it is not shown on any of the photographs obtained. The members of this group, like the others in which the p^2 terms appear, show large displacements towards the red when the pressure in the vacuum tubes is relatively high. The above wave-numbers have been deduced from wave-lengths measured in low-pressure tubes.

Singlets.

A singlet term is indicated by the following pair of lines (Nos. 1 and 2, Plate 1):—

d_3		d_2		
(1)		(2)		j
17333·83(2)	*60·77*	17394·60(3)	P	(1)

$$P = 69888\cdot51.$$

A singlet P term is obviously the most appropriate for this combination, Pd_1 being then ruled out by consideration of inner quantum numbers. The P term, it will be observed, is only a trifle smaller than the p_1 term.

The P term appears also in combination with the p' terms, producing an inverted triplet which is clearly shown on the photographs (No. 3, Plate 1), although the lines are of no great intensity. Thus:—

p'_3		p'_2		p'_1		
(0)		(1)		(2)		j
21384·50(2)	*35·28*	21419·78(2)	*58·49*	21478·27(2)	P	(1)

A faint line at λ 5073·5 appears to represent the combination Ps; thus, P—s = 19704·21, as compared with the observed wave-number 19704·59(1).

The groups of lines so far described include a majority of the chief lines, and several of the fainter ones, in the region λ6650–λ3300. There are, however, a number of lines which do not occur in groups and doubtless belong to a singlet system. Four of the more important lines, beginning with λ 3995, certainly involve two of the terms which have already been deduced. The associated terms are singlets of S type ($j = 0$). Thus:—

$$\left.\begin{array}{l} 25024\cdot27(10) = P - S \\ 25271\cdot88(5) = p_2 - S \end{array}\right\} \qquad S = 44864\cdot36.$$

$$\left.\begin{array}{l} 29085\cdot46(6) = P - S^2 \\ 29333\cdot17(3) = p_2 - S^2 \end{array}\right\} \qquad S^2 = 40803\cdot12.$$

These combinations are in complete accordance with the azimuthal and inner quantum conditions. It does not seem possible, however, to regard S and S^2 as consecutive terms of a simple Rydberg sequence because there is no line corresponding with the next following term. The spectrum in this region is, in fact, very simple, the only other prominent singlets in the region λ4000–λ3000 being λ3919·003(6) and λ3006·86(7). The latter ($\nu = 33247 \cdot 67$) is possibly the PD line, and we may write—

$$D? = 69888 \cdot 51 - 33247 \cdot 67 = 36640 \cdot 84.$$

Other Regularities.

Two pairs of lines with apparently equal separations have been noted by Ruark, and a similar pair has been found in the course of the present investigation. The wave-numbers and separations are as follows :—

18190·37(3*n*)	*51·78*	18248·57(1*n*)
23595·04(4*n*)	*51·64*	23646·68(2*n*)
24723·84(2*n*)	*51·78*	24775·62(4*n*)

The separation suggests identity with Δp^2_{23}, but the connection is not clear.

The p′ and d′ terms.

The significance of such terms as p' and d' is not yet completely understood, but evidence has been adduced in favour of the view that they involve the simultaneous transitions of two electrons, with the emission of a single quantum of energy. Russell and Saunders,[*] and Wentzel[†] have found that pp' multiplets of calcium form a series of approximately Rydberg type, and converge to a limit which is higher than that of the normal series of triplets, so that some of the terms become negative. This is regarded as an indication of the emission of a greater amount of energy in the pp' transitions than could be supplied by the series electron alone, and it may be supposed that the deficiency is made good by a transition of the second valence electron.

The terms p', d', &c., which are thus possibly associated with the simultaneous transitions of two electrons may be distinguished from corresponding terms of ordinary type by a further selection rule to which attention has been directed by Laporte in his discussion of the arc spectrum of iron.[‡] In the case of iron it would appear that in the combination of ordinary and "double-transition" terms, the usual selection rule for azimuthal quantum numbers ($\Delta k = \pm 1$)[§] is to be replaced by the rule $\Delta k = 0$, while $\Delta k = \pm 1$ is forbidden. This rule is probably also applicable to the spectrum of N II as illustrated in fig. 2, which is drawn on the plan adopted by Laporte.

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[*] 'Science,' vol. 59, p. 50 (1924).

[†] 'Phys. Zeit.,' vol. 25, p. 182 (1924).

[‡] 'Zeit. f. Phys.,' vol. 23, p. 166 (1924); vol. 26, p. 17 (1924).

[§] $k = 1$ for s, 2 for p, 3 for d, and so on.

$$\begin{tikzcd}
S, S^2, s \arrow[r, leftrightarrow] & P, p, p^2 \arrow[r, leftrightarrow] \arrow[d, leftrightarrow] & D, d \arrow[d, leftrightarrow] \\
 & p' \arrow[r, leftrightarrow] & d'
\end{tikzcd}$$

FIG. 2.—Illustrating combinations of ordinary and "double-transition" terms in N II.

The combinations to be expected in accordance with the new rule, having due regard for the inner quantum number restrictions, are those indicated by arrows, it being further understood that terms which are placed in the same group do not combine with each other. All the combinations which have so far been recognised in N II are in accordance with the diagram, but some of the possible combinations would yield lines outside the range of the present observations, so that their presence or absence cannot be checked. The combination pd' would fall in an observed region and definitely does not occur in N II.

The second p term behaves in combination like the first, and it has accordingly been temporarily designated p^2 in preference to p''; the second S term has similarly been called S^2. If p and p^2 were the consecutive terms $2p$ and $3p$ of an ordinary Rydberg sequence, $2p$ would have a value about 97,000, and the corresponding value of $1p$ would be of the order of 300,000, which is far above that suggested by astrophysical data. It seems probable that the terms do not conform closely with a Rydberg formula.

Combinations and Relative Term-values.

The combinations which have been identified, and the relative values of the various terms, are collected in Table II. The combinations are stated in the order in which they have been described, and the terms are arranged in order of magnitude, p_1 being assumed as 70,000. Under k and j are the azimuthal and inner quantum numbers respectively.

It results from the foregoing investigation that the largest term is a p term, and from this it may be concluded that in the atom of N II the series electron normally occupies a 2_2 orbit. As expressed in the "spectroscopic displacement law," other investigations have shown that the spectrum of an ionised element is of the same character as that of the neutral atom of the element which immediately precedes it in the periodic table, and it follows that there is a close similarity in the arrangement of the electrons in the two atoms. The

Table II.—List of Combinations and Term-values.

Combinations.

$p - p'$
$p - d$
$p - s$
$d - d'$
$p' - d'$
$p' - p^2$
$s - p^2$
$d - p^2$
$\mathrm{P} - d_{23}$
$\mathrm{P} - p'$
$\mathrm{P} - s$
$\mathrm{P} - \mathrm{S}$
$p_2 - \mathrm{S}$
$\mathrm{P} - \mathrm{S}^2$
$p_2 - \mathrm{S}^2$
$\mathrm{P} - \mathrm{D}?$

Relative Terms.

k	j		
2	(0)	$p_3 = 70167\cdot96$	$\Delta p_{23} = 31\cdot60$
	(1)	$p_2 = 70136\cdot36$	$\Delta p_{12} = 136\cdot36$
	(2)	$p_1 = 70000\cdot00$	
2	(1)	$\mathrm{P} = 69888\cdot51$	
3	(1)	$d_3 = 52554\cdot74$	$\Delta d_{23} = 61\cdot01$
	(2)	$d_2 = 52493\cdot73$	$\Delta d_{12} = 96\cdot06$
	(3)	$d_1 = 52397\cdot67$	
1	(1)	$s = 50184\cdot30$	
2	(0)	$p'_3 = 48503\cdot95$	$\Delta p'_{23} = 35\cdot25$
	(1)	$p'_2 = 48468\cdot70$	$\Delta p'_{12} = 58\cdot37$
	(2)	$p'_1 = 48410\cdot33$	
1	(0)	$\mathrm{S} = 44864\cdot36$	
1	(0)	$\mathrm{S}^2 = 40803\cdot12$	
3	(2)	$\mathrm{D}? = 36640\cdot84$	
3	(1)	$d'_3 = 31638\cdot75$	$\Delta d'_{23} = 24\cdot09$
	(2)	$d'_2 = 31614\cdot66$	$\Delta d'_{12} = 30\cdot29$
	(3)	$d'_1 = 31584\cdot37$	
2	(0)	$p^2{}_3 = 22536\cdot22$	$\Delta p^2{}_{23} = 51\cdot75$
	(1)	$p^2{}_2 = 22484\cdot47$	$\Delta p^2{}_{12} = 119\cdot42$
	(2)	$p^2{}_1 = 22365\cdot05$	

conclusion with regard to ionised nitrogen is therefore of additional interest as giving an indication of the structure of the neutral atom of carbon, the spectrum of which has not yet been resolved into series. The first group of elements in

Bohr's table of atomic structures* may accordingly now be extended to carbon with considerable confidence. Thus, in the neutral atom of carbon it is probable that there are two electrons in 1_1 orbits, two in 2_1 and two in 2_2 orbits.

Summary.

New observations of the second line spectrum of nitrogen (N II, or N^+) have been made in the region λ 6650–λ 2200, and 52 lines have been classified in relation to the terms which combine to produce them. In this region, all the terms which have been identified belong to singlet or triplet systems. These have been found to combine with each other in agreement with the selection rules applicable to other spectra in which p' and d' terms appear. The absolute values of the terms cannot yet be stated, but a value of 70,000 has been provisionally assigned to $2p$, in accordance with the value suggested for $1p$ by astrophysical data.

The largest term identified is a p term, and it may be inferred that the series electron in singly-ionised nitrogen normally occupies a 2_2 orbit, so that the atom of N II has two electrons in 1_1 orbits, two in 2_1 and two in 2_2 orbits. From the spectroscopic displacement law it may be further inferred that this is also the probable arrangement of orbits in the neutral atom of carbon, the spectrum of which has not yet been resolved into series.

Three groups of lines which involve one of the p terms are remarkable as showing large displacements ($> 0{\cdot}5$A) to the red in vacuum tubes at relatively high pressures.

The author has pleasure in acknowledging his indebtedness to Mr. J. Brooksbank and Mr. L. J. Freeman for some of the photographs which have been utilised in the foregoing investigation.

DESCRIPTION OF PLATE 1.

1. Spark spectrum of copper in air } 10 feet concave grating.
2. Spark spectrum of iron in air }

These show the groups $p'd'$, Pd, and pd.

3. Nitrogen vacuum tube, large Littrow prismatic spectrograph. Shows the combination groups dd', Pp', pp'. The short lines near the edges of the spectrum are arc lines of iron.
4. Nitrogen vacuum tube, large quartz spectrograph. Shows the lines PS, p_2S, and the groups pp' and sp^2. Lines of N III at λλ 4641·90, 4640·64, 4634·16 appear faintly.
5. Nitrogen vacuum tube, large quartz spectrograph. Shows the lines PS^2, p_2S^2, and the groups sp^2 and dp^2.

The bands of nitrogen which appear in 4 and 5 are mainly due to the use of an end-on tube, the bands originating in the wider part of the tube. The bright place on the red side of the strong line λ 3995 is the head of a band, λ 3998. There is also a faint band head at λ 3582 which might be mistaken for a line in the reproduction.

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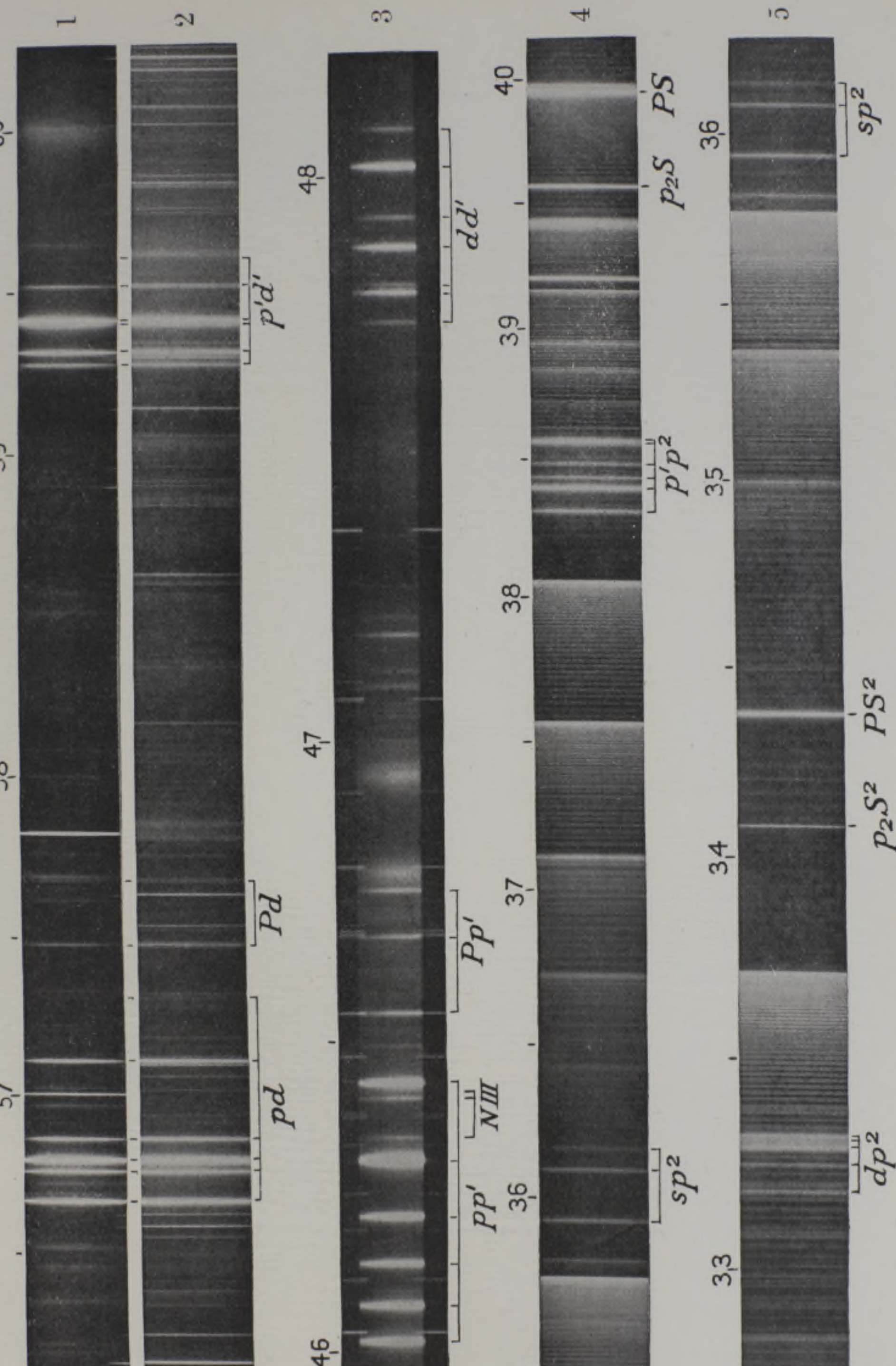
* 'Ann. d. Phys.,' vol. 71, p. 260 (1923).



1. Cu spark in air. 2. Fe spark in air. 3, 4, 5. Nitrogen Vacuum tube.

(*Facing p.* 42)

results are of significance in connection with the mechanism of catalytic hydrogenation.

In conclusion, the author wishes to express his gratitude to Prof. K. T. Compton and Prof. H. S. Taylor for their constant encouragement, advice and assistance. He also welcomes the opportunity to thank all the research workers in Palmer Physical Laboratory, Princeton, whose friendly help was so generously given at all times.

The Spectrum of Ionised Oxygen (*O II*).

By A. Fowler, F.R.S., Yarrow Research Professor of the Royal Society, Imperial College, South Kensington.

(Received December 23, 1925.)

Two different line spectra of oxygen have long been known under the names "compound line" and "elementary line" spectra, assigned by Schuster in 1879* on the supposition that complex and simplified molecules or "molecular groupings" were respectively involved in their production. The possibility of a further modification of the line spectrum was also foreshadowed by Schuster, in collaboration with Roscoe,† in the observation of a line at λ 5592 when a condensed discharge was passed through oxygen in a short and narrow capillary tube. Additional lines of this third type were observed later by Lunt,‡ and further investigated by Fowler and Brooksbank.§

In accordance with present views as to the origin of spectra, the three spectra are attributed to neutral, singly-ionised, and doubly-ionised atoms, and are designated O I, O II, O III, or O, O^+, O^{++}. Other spectra representing higher degrees of ionisation are theoretically possible, and evidence of the production of O IV and O V in the spectra of vacuum sparks has been obtained by Millikan and Bowen.* The first three spectra are of considerable interest to astrophysicists on account of their occurrence in stars of successively higher temperatures, in strict accordance with the results of laboratory experiments. Among other points of interest, the analysis of these spectra may eventually lead to trustworthy values of the successive ionisation potentials, and thence to important deductions as to stellar temperatures. This result, however, has only at present been finally attained with respect to O I, through the extension of the observations into the extreme ultra-violet by Hopfield.†

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* 'Phil. Trans.,' vol. 170, p. 41 (1879).

† 'Mem. Phil. Soc. Manchester,' 3rd Series, vol. 7, p. 82 (1880).

‡ 'Annals of the Cape Observatory,' vol. 10, pt. II, p. 26B (1906).

§ 'Monthly Notices R.A.S.,' vol. 77, p. 511 (1917).

Some of the regularities in the spectrum of O II have already been recognised by the present author‡ and by Croze,§ the latter partly with the aid of his earlier observations of the spectrum with the source in a magnetic field.||

The present paper gives the results of new measurements of the lines of O II in the region λ 6750 to λ 1950, together with details of the numerous additional regularities which have been traced. An extension to shorter wavelengths is contemplated, and the structure of the third spectrum is also under investigation.

Observational Data.

Lines attributed to O II are conspicuous in the ordinary spark in air, but under these conditions they are mostly too broad for accurate measurements. Most of the measurements have accordingly been made on photographs of the spectrum of the discharge in vacuum tubes, where the conditions could be so controlled as to produce a majority of the lines with the desired sharpness. The O II lines were produced by condensed discharges of moderate intensity through capillary tubes, and could be readily distinguished from the lines of O III, which were added to the spectrum as the pressure was lowered and the intensity of the discharge increased.

Several spectrographs were employed in the investigation, but all were of adequate dispersion and resolving power for the particular regions under examination with them. Thus, for the visual spectrum, most of the photographs were taken with a large Littrow glass spectrograph, giving a dispersion ranging from 10 A per mm. at λ 5900 to 1·9 A per mm. at λ 4000. For the

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* 'Phys. Rev.,' Sept., 1924, p. 209. 'Proc. Nat. Acad. Sci., Washington,' vol. 11, p. 329 (1925).

† 'Astrophys. Journ.,' vol. 59, p. 114 (1924).

‡ 'Report on Series in Line Spectra,' p. 167 (1922).

§ 'Comptes Rendus,' vol. 180, pp. 277 and 432 (1925).

|| 'Ann. de Physique,' vol. 1, p. 80 (1914).

ultra-violet, a large quartz spectrograph (Hilger's E 1) was employed, giving 12 A per mm. at λ 4000 and 2 A per mm. at λ 2300. Many measurements were also made on photographs taken in the first order of a 10-ft. concave grating, giving about 5½ A per mm., and of many of the stronger lines on third order plates. For the region λ 2280—λ 1850, a small quartz spectrograph by Bellingham and Stanley was used, giving 9·8 A per mm. at λ 2280 and 4·8 A per mm. at λ 1850.*

Relative accuracy over moderate ranges, it may be remarked, is not difficult to obtain, but on account of the long exposures required to bring out some of the lines, and the consequent liability to displacements arising from temperature changes, the absolute values are less certainly reached. The analysis of the spectrum, however, provides a check on the values obtained for some of the lines. In view of the great labour required to establish wave-lengths to seven figures, most of them are given to six figures.

The wave-lengths of some of the stronger lines in the blue and violet had previously been determined with great care, under the present author's direction, by J. S. Clark.† With two exceptions these have been verified to at least the second decimal place, and have been used as standards for the measurement of fainter intermediate lines on some of the photographs.

An effort has been made to record the spectrum as completely as possible, because faint lines are frequently of importance for the completion of multiplet groups. Care has also been taken to exclude lines due to carbon or to oxygen at stages of ionisation higher than the first. Pending a more complete investigation of the various spectra of carbon, however, it is not quite certain that every line of this element has been eliminated.

Description of Table I.

The wave-lengths (international scale) of all the lines which are believed to be due to O II are collected in Table I. The figures in brackets following the wave-lengths in column 1 indicate approximate relative intensities in the usual manner. Lines which have a tendency to become diffuse are indicated by the letter *n* attached to the intensity number. A few groups of lines show a broadening and displacement towards the red under some conditions, and are distinguished by the letter *r*; the tabulated wave-lengths of such lines were determined from plates taken with the gas at moderate or low pressures.

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* The author is indebted to the Government Grant Committee for this instrument.

† 'Astrophys. Journ.,' vol. 40, p. 333 (1914).

The third and fourth columns of the table indicate the classification of the lines, as explained later. Next follow the observations of Exner and Haschek, Lunt and Schniederjost, and some of those by Eisig, as quoted by Kayser,* but omitting lines which appear to belong to O III. These wave-lengths have been corrected to the international scale. In the earlier part of the table only the lines of Eisig which are not included by the other observers are noted. It will be observed that the number of lines attributed to O II has been greatly increased by the present observations.

Two groups of lines, λ 3048—λ 2992 and λ 2918—λ 2885, which have not yet been classified, are remarkable for their diffuseness in most of the photographs which have been obtained. Approximate measures of these lines in the diffuse state are given in the column of remarks, while those in the first column are of fairly well-defined lines in a particular photograph, which are believed to correspond with the diffuse lines.

An isolated narrow triplet in the ultra-violet has been omitted from the table, namely :—

λ		ν	Δν
3218·04	(3)	31065·87	
			12·56
3216·74	(2)	31078·43	
			7·05
3216·01	(2)	31085·48	

The separations appear to be identical with those of two inverted triplets at λλ 6264 and 5410, which have been assigned by Runge and Paschen to O I.† The triplet is, therefore, probably due to O I, as is also a similar triplet in the extreme red, λ 8221, observed by Merrill, Hopper and Keith.‡

The number of lines entered in the table, extending from the red to λ 1956 in the far ultra-violet is about 400. Of these, 90 have been classed as belonging to the doublet system, and 68 to the quartet system, including the majority of the stronger lines, and many of the fainter ones. Further analysis of the data may be expected to lead to the recognition of other regularities.

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* 'Handbuch der Spectroscopie,' vol. VI, p. 214.

† Fowler's 'Report on Series,' p. 169.

‡ 'Astrophys. Journ.,' vol. 54, p. 76 (1921).

Table I.—Lines of Ionised Oxygen (O II, or O $^+$).

λ, Intensity.	ν	Combinations.		Other Observations.		Remarks.
		Doublet.	Quartet.	Exner and Haschek.	Lunt.	
6721·35 (5)	14873·87	$2p_2-2s_1$				
6654·77 (1)	15022·68					
6640·90 (4)	15054·05	$2p_1-2s_1$				
5206·73 (5)	19200·58	$ap'_2-ap''_2$				
5190·56 (3)	19260·40	$ap'_1-ap''_2$				Isolated group.
5176·00 (2)	19314·57	$ap'_2-ap''_1$				
5160·02 (4)	19374·39	$ap'_1-ap''_1$				
4955·78 (3)	20172·84	$ap'_2-bd'_2$			5·83 (1)	$^2p'\ ^2d'$ identified by Cr
4943·06 (7)	20224·76	$ap'_2-bd'_3$			3·27 (6)	
4941·12 (5)	20232·70	$ap'_1-bd'_2$			1·04 (4)	
4924·60 (6)	20300·57				4·77 (6)	
4906·88 (5)	20373·87				7·09 (5)	
4890·93 (4)	20440·31				0·87 (3)	
4871·58 (5)	20521·50	$bp'_2-cd'_3$			1·70 (4)	
4864·95 (3)	20549·47				5·10 (1)	
4861·03 (3)	20566·04	$bp'_1-cd'_2$			1·12 (3)	
4856·82 (3)	20583·38		$s_2-d'_{21}$		7·01 (4)	
4856·49 (2)	20585·27		$s_2-d'_3$			
4845·01 (1)	20634·04		s_2-x_3		} 4·26 (2d)	Possibly double.
4843·26 (1n)	20641·50					
4752·70 (2)	21034·81				2·96 (0)	
4751·34 (4)	21040·83				1·59 (4)	
4744·85 (0)	21069·61					
4741·71 (3)	21083·56				2·12 (3)	
4710·04 (5)	21225·31			10·1 (1)	09·79 (2)	
4705·36 (8)	21246·43			5·38 (2)	5·14 (6	
4703·18 (3)	21256·28					Eisig 03·2 (1)
4701·76 (0)	21262·70	$bp'_2-bp''_1$				
4701·23 (2)	21265·10	$bp'_2-bp''_2$				Eisig 01·3 (1)
4699·21 (7)	21274·23			9·21 (2)	9·01 (5)	
4696·36 (2)	21287·15		ap_3-d_2			$^4p\ ^4d$ identified by Cr
4691·47 (1)	21309·33	$bp'_1-bp''_1$				
4690·97 (0)	21311·60	$bp'_1-bp''_2$				
†4676·246 (8)	21378·70		ap_3-d_3	6·16 (2)	6·04 (5)	†=λ Clark.
4673·75 (4)	21390·12		ap_2-d_1		3·71 (0)	
4669·53 (0)	21409·46					
†4661·650 (9)	21445·64		ap_2-d_2	1·58 (2)	1·46 (5)	
†4650·853 (6)	21495·43		ap_1-d_1	0·82 (2)	0·77 (5)	
†4649·148 (10)	21503·32		ap_3-d_4		8·88 (9)	
†4641·827 (9)	21537·23		ap_2-d_3	1·76 (3)	1·66 (8)	
†4638·865 (6)	21550·98		ap_1-d_2	8·81 (2)	8·70 (5)	
4610·14 (3n)	21685·27					
4609·42 (4n)	21688·65			9·55 (1)	9·22 (2)	
4602·11 (2n)	21723·11				2·20 (0)	
†4596·189 (8)	21751·08			6·13 (3)	5·87 (7)	} $\Delta\nu = 24\cdot68$.
†4590·983 (9)	21775·76			0·95 (3)	0·73 (8)	
4506·50 (2n)	22183·97					
4491·25 (3n)	22259·29				1·04 (0)	
4489·48 (1n)	22268·07					
4488·09 (2n)	22274·97					
4487·72 (0n)	22276·80					

Table I—continued.

tensity.	ν.	Combinations.		Other Observations.		Remarks.
		Doublet.	Quartet.	Exner and Haschek.	Lunt.	
88 (2n)	22325·75					
2 (3)	22368·51			9·38 (1)	9·31 (2)	
8 (4)	22375·72			7·89 (2)	7·71 (3)	
5 (1)	22377·37					
(2n)	22383·54				} 5·80 (4d)	Eisig 66·5 (1).
0 (4)	22388·14			5·37 (2)		
8 (6)	22453·62	$2p_2-ad_2$		2·40 (2)	2·24 (3)	$^2p^2d$ identified by Croze.
1 (6)	22474·66				8·10 (3)	
8 (1)	22480·37					
5 (5)	22500·76			3·12 (1)	3·01 (2)	
74 (8)	22633·60	$2p_1-ad_2$		6·97 (5)	6·85 (9)	† = λ Clark.
8 (10)	22644·29	$2p_2-ad_3$		4·90 (8)	4·91 (10)	
(1)	22689·86	$ad_3-bd'_2$				
5 (7)	22741·84	$ad_3-bd'_3$		5·97 (2)	5·87 (3)	
5 (2n)	22827·00					
0 (3n)	22833·00					
5 (0n)	22844·74					
(2n)	22868·25					
(4)	22880·66	$ad_2-bd'_2$		9·31 (1)	9·19 (2)	
06 (7)	22893·09		$ap_3-p'_2$	6·87 (3)	6·86 (6)	$^4p^4p'$ identified by Croze.
8 (1)	22932·62	$ad_2-bd'_3$				
0 (0)	22937·77					
5 (0)	22943·83					possibly double.
0 (1n)	22963·06					
75 (6)	22975·33	ad'_3-bd_3		1·37 (3)	1·18 (7)	
35 (8)	22985·05		$ap_3-p'_3$	9·41 (6)	9·36 (8)	
29 (5)	22995·66	ad'_2-bd_2		7·42 (2)	7·38 (6)	
70 (7)	23005·50		$ap_2-p'_1$	5·55 (3)	5·59 (6)	
2 (0n)	23011·58					
0 (00)	23017·52					
0 (4n)	23024·42				1·85 (3)	
6 (2n)	23033·11				0·34 (2)	
6 (6)	23051·70		$ap_2-p'_2$	6·85 (2)	6·75 (3)	
9 (0n)	23065·4					
6 (1n)	23073·51					
9 (2)	23078·15	$bd_2-cd'_2$			1·80 (0)	
7 (0)	23080·38	$bd_2-cd'_3$				
1 (0n)	23081·8			1·07 (1)		
2 (2)	23095·58	$bp'_2-bs'_1$		8·54 (1)	8·72 (0)	
89 (0)	23099·47	$bd_3-cd'_2$				
48 (3)	23101·66	$bd_3-cd'_3$		7·45 (1)	7·42 (2)	
77 (3)	23110·80		$ap_1-p'_1$	5·69 (1)	5·74 (1)	
93 (1)	23142·04	$bp'-bs'_1$				λ approx.
647 (8)	23143·55		$ap_2-p'_3$	9·62 (3)	9·63 (6)	
160 (8)	23156·88		$ap_1-p'_2$	7·11 (3)	7·09 (6)	
55 (0n)	23165·53					
43 (1n)	23176·91					
10 (0n)	23184·06					
96 (1n)	23200·95					
31 (1n)	23209·84					
53 (0)	23219·54					
82 (5n)	23228·66			3·58 (1n)	3·61 (3)	
00 (0n)	23233·09					

Table I—continued.

λ, Intensity.	ν.	Combinations.		Other Observations.		Remarks.
		Doublet.	Quartet.	Exner and Haschek.	Lunt.	
4294·82 (3*n*)	23277·34				4·89 (2)	
4292·23 (0*n*)	23291·38				2·27 (0)	
4291·25 (1*n*)	23296·70				1·29 (1)	
4288·83 (1*n*)	23309·85				8·86 (0)	
4285·70 (3*n*)	23326·87				5·72 (1)	
4283·75 (0*n*)	23337·50				3·65 (0)	
4282·96 (1*n*)	23341·80				3·05 (0)	
4281·40 (0*n*)	23350·30					
4277·90 (1*n*)	23369·40				7·70 (0)	
4277·40 (1*n*)	23372·13					
4276·71 (1*n*)	23375·92				6·72 (1)	
4275·52 (4*n*)	23382·40				5·61 (3)	
4273·17 (0*n*)	23395·27					
4253·98 (8*n*)	23500·80			3·58 (1*n*)	4·08 (4)	
4196·72 (1)	23821·44	$bd_2—bp''_1$			6·72 (0)	
4192·50 (2)	23845·42	$bd_3—bp''_2$			2·60 (0)	
†4189·793 (10)	23860·82			9·90 (7)	9·92 (8)	$\Delta\nu = 24·75$.
†4185·453 (8)	23885·57			5·56 (6)	5·54 (8)	
4169·23 (4)	23978·50			9·33 (2)	9·27 (3)	
4156·54 (3)	24051·70			6·67 (1)	6·60 (1)	
†4153·310 (7)	24070·42				3·48 (6)	
4146·09 (3)	24112·33				6·15 (3)	
4145·90 (0)	24113·44					
4143·77 (2)	24125·84			3·74 (1)	3·79 (3)	
4143·52 (1)	24127·29					
4142·24 (0)	24134·74			2·21 (1)	2·22 (2)	
4142·00 (1)	24136·14					
4140·74 (0)	24143·49					
4132·82 (6)	24189·74			2·87 (2)	2·91 (5)	32·99 Clark (“unsa factory”).
4129·34 (2)	24210·14			9·45 (1)	9·47 (0)	
4121·48 (4)	24256·31			1·58 (2)	1·49 (2)	
4120·55 (2)	24261·78		$p'_3—d'_2$	0·47 (3)	0·46 (6)	$^4p'^4d'$ partially ident by Croze.
4120·30 (3)	24263·25		$p'_3—d'_3$			20·267 Clark.
†4119·222 (8)	24269·61		$p'_3—d'_4$	9·31 (8)	9·36 (8)	
4113·82 (1)	24301·48			4·05 (1)	3·92 (0)	
4112·04 (4)	24312·00		$p'_3—x_3$	2·11 (2)	2·07 (3)	
4110·80 (3)	24319·33			0·91 (2)	0·80 (3)	
4110·20 (1)	24322·88					
4108·75 (0*n*)	24331·46					
4107·07 (1*n*)	24341·41				7·12 (0)	
4106·03 (0)	24347·57		$d_4—f_3$			$^4d^4f$ partially ident by Croze.
†4105·001 (7)	24353·68		$p'_2—d'_2$	5·00 (5)	5·00 (6)	
4104·74 (5)	24355·24		$p'_2—d'_3$			
4103·01 (5)	24365·51				3·09 (2)	
4098·27 (0*n*)	24393·68				8·28 (1)	
4097·32 (1)	24399·34		$p'_1—d'_1$		7·28 (4)	
4097·25 (4*n*)	24399·76		$p'_1—d'_2$			
4096·54 (3)	24403·98		$p'_2—x_3$		6·50 (2)	
4095·63 (0*n*)	24409·40				5·76 (1)	
4094·18 (0)	24418·05		$d_3—f_2$			
4092·94 (5)	24425·45		$d_4—f_4$	3·00 (3)	2·96 (4)	

Table I—continued.

nsity.	ν.	Combinations.		Other Observations.		Remarks.
		Doublet.	Quartet.	Exner and Haschek.	Lunt.	
(4n)	24447·31			9·08 (2)	9·28 (5)	
(2n)	24459·98				7·18 (2)	
(3)	24472·20		d_3-f_3	5·21 (3)	5·17 (5)	
(1)	24474·95				4·01 (2)	
(2n)	24479·51					
(0)	24508·91					
(4)	24509·74		d_2-f_2	8·96 (2)	8·86 (4)	
(10)	24527·74		d_4-f_5	5·93 (10)	5·94 (10)	† = λ Clark.
(8)	24550·11		d_3-f_4	2·25 (10)	2·30 (10)	
(0)	24555·88					
(6)	24563·70		d_2-f_3	9·89 (10)	9·92 (10)	
(4)	24565·31		d_1-f_2			
(1n)	24606·04				3·08 (0)	
(2n)	24617·67				0·92 (1)?	
(3n)	24620·09					
(0n)	24656·41					
(1n)	24695·26				8·40 (0)	
(0n)	24738·16					
(0n)	24776·17					
(0n)	24829·09					
(1n)	24843·65					
(0n)	24856·87					
(0)	25084·70					
(5)	25101·37	$2p_2-ap'_1$		2·75 (2)	2·78 (6)	${}^2p^2p'$ identified by Croze.
(10)	25161·12	$2p_2-ap'_2$		3·29 (8)	3·36 (9)	
(1)	25198·07					
(0)	25225·46					
(7)	25281·36	$2p_1-ap'_1$		4·40 (4)	4·49 (7)	
(5)	25341·10	$2p_1-ap'_2$		5·10 (3)	5·11 (6)	45·033 Clark.
(6)	25507·70	$ad'_2-bp'_1$			9·36 (6)	3rd order grating.
(2)	25554·59	$ad'_2-bp'_2$				,, ,,
(10)	25555·48	$ad'_3-bp'_2$		2·05 (3)	2·04 (7)	,, ,,
(4)	25584·92			7·58 (1)	7·49 (0)	
(1)	25658·13					
(2)	25677·05					
(3)	25745·02		$d_4-d'_3$		3·16 (0)	${}^4d^4d'$ partially identified by Croze.
(1)	25749·66					
(7)	25751·37		$d_4-d'_4$	2·32 (3)	2·22 (6)	
(4)	25793·70		d_4-x_3			
(2)	25805·16					
(1)	25816·15					
(1)	25868·06		$d_3-d'_2$			
(5)	25869·59		$d_5-d'_3$	4·59 (1)	4·55 (1)	
(2)	25875·96		$d_3-d'_4$	3·55 (1)	3·56 (0)	
(4)	25918·35		d_3-x_3		7·22 (0)	
(5)	25925·21				6·19 (0)	
(2)	25956·05			1·35 (1)		
(3)	25959·69		$d_2-d'_{21}$		1·03 (0)	
(2)	25961·22		$d_2-d'_3$			
(3)	25980·92			8·03 (1)		
(3)	26010·05		d_2-x_3			
(3)	26015·20		$d_1-d'_{21}$			

Table I—continued.

λ, Intensity.	ν.	Combinations.		Other Observations.		Remarks.
		Doublet.	Quartet.	Exner and Haschek.	Lunt.	
3838·41 (0)	26045·10					N ?
3833·10 (3)	26081·18					
3830·45 (4r)	26099·22	$ap'_2—3p_1$				The lines marked sometimes bro and displaced t the red.
3821·68 (4r)	26159·10	$ap'_1—3p_1$				
3803·14 (6r)	26286·63	$ap'_2—3p_2$			3·01 (0)	
3794·48 (3r)	26346·52	$ap'_1—3p_2$				
3785·01 (0n)	26412·53					
3777·60 (4r)	26464·35		$s_2—bp_1$			
3762·63 (5r)	26569·63		$s_2—bp_2$		2·47 (0)	
3749·49 (9)	26662·74		$ap_3—s_2$	9·51 (5)	9·48 (7)	$^4p^4s$ identified by P
3746·77 (0)	26632·10					
3741·82 (0n)	26717·40					
3739·92 (6r)	26730·98		$s_2—bp_3$		9·80 (0)	
3735·94 (3)	26759·43	$bp'_2—dd'_{32}$				
3732·07 (0)	26787·20					
3729·34 (2)	26806·78	$bp'_1—dd'_{32}$				
3727·33 (8)	26821·26		$ap_2—s_2$	7·32 (4)	7·34 (6)	
3712·75 (7)	26926·58		$ap_1—s_2$	2·80 (2)	2·72 (5)	
3533·97 (00n)	28288·7					
3516·92 (0n)	28425·9					
3506·02 (0n)	28514·2					
3501·67 (00n)	28549·7					
3500·5 (00n)	28559·2					
3496·32 (2)	28593·35					
3495·44 (0n)	28600·5					
3494·66 (00n)	28606·9					
3488·23 (1)	28659·66					
3485·45 (0n)	28682·5					
3478·43 (0n)	28740·4					
3474·94 (1)	28769·27					
3470·81 (8)	28803·50	$ad_3—3p_2$		0·93 (1) ?		
3470·42 (5)	28806·74	$ad_2—3p_1$				
3459·07 (0n)	28901·2					
3457·99 (1n)	28910·3					
3453·31 (0n)	28949·4					
3447·98 (5)	28994·21	$ad_2—3p_2$				
3420·61 (3n)	29226·21					
3419·87 (2n)	29232·53					
3409·84 (6r)	29318·50	$bd_2—dd'_{32}$			Eisig. 10·1 (2)	Sometimes broad and displaced to red.
3407·38 (7r)	29339·68	$bd_3—dd'_{32}$			7·6 (2)	
3390·25 (8)	29487·92	$s_1—ap''_2$		0·29 (2n)	0·1 (4)	
3377·20 (7)	29601·86	$s_1—ap''_1$		7·19 (1)	7·0 (3)	
3375·77 (0)	29614·4					
3374·77 (00)	29623·2					
3371·85 (2n)	29648·8					
3370·23 (00n)	29663·1					
3367·00 (00n)	29691·5					
3360·15 (00n)	29752·0					
3306·60 (6r)	30233·87		$p'_2—bp_1$			The whole group 3306 to 3270 is s times broadened displaced toward red.
3305·15 (6r)	30247·13		$p'_3—bp_2$			
3301·56 (3r)	30280·03		$p'_1—bp_1$			
3295·13 (4r)	30339·12		$p'_2—bp_2$			
3290·13 (5r)	30385·22		$p'_1—bp_2$			

Table I—continued.

ensity	ν.	Combinations.		Other observations.		Remarks.
		Doublet.	Quartet.	Exner and Haschek.	Eisig.	
9 ($9r$)	30408·68		p'_3-bp_3		7·7 (1)	
9 ($7r$)	30500·53		p'_2-bp_3			
($7r$)	30539·39				3·8 (1)	
($7r$)	30563·09				1·1 (1)	
0)	31290·9					
n)	31544·6					
n)	31585·5					C ?
($4r$)	31840·27		d_2-bp_1	9·32 (1)		All the lines of this group are sometimes broadened and displaced towards the red.
($8r$)	31853·78		d_3-bp_2		8·5 (1)	
($10r$)	31890·56		d_4-bp_3	5·2 (1)	4·8 (2)	
$3r$)	31895·64		d_1-bp_1			
$7r$)	31945·37		d_2-bp_2			
$2r$)	32000·82		d_1-bp_2			
($6r$)	32015·14		d_3-bp_3			
$1r$)	32106·75		d_2-bp_3			
($1n$)	32274·9					
$2n$)	32442·8					
[illegible]	32799·0					3048·0* (see footnote).
1)	32887·8					3040·0
1)	32890·5					
1)	32966·5					3032·4
2)	32971·1					
1)	33006·6					3029·0
1)	33040·1					3026·0
1)	33148·3					3016·0
1)	33163·3					3013·7
3)	33175·8					
1)	33181·7					
($1d$)	33214·8					3010·0
(3)	33226·6					Also O III here.
(1)	33232·0					3008·8
(3)	33245·2			07·30 ($2n$)		3007·1
(3)	33248·1					
(2)	33256·7					3006·0
(2)	33261·4					
(1)	33291·1					3003·0
(3)	33349·2					2997·7 also O III here.
(1)	33369·4					2996·1
(3)	33406·5					2992·5* Also C line here.
88 ($2n$)	33970·4					
				Schnieder-jost.		
65 ($1n$)	34287·7					2915·7§ (see footnote).
76 ($3n$)	34333·5					2911·9
14 ($2n$)	34340·8					O ?
74 ($1n$)	34369·1					2908·8
56 ($4n$)	34394·9					2906·6
00 ($2n$)	34413·4					2905·3
30 ($2n$)	34421·7					2904·2
30 ($0n$)	34469·1					2900·4
53 ($1n$)	34502·1					2897·7
62 ($2n$)	34548·7					2893·4

Table I—continued.

λ, Intensity.	ν.	Combinations.		Other Observations.		Remarks.
		Doublet.	Quartet.	Schneiderjost.	—	
2887·85 (3*n*)	34617·7					2888·0
§2885·90 (1*n*)	34641·1					2885·9§
2883·78 (3)	34666·6					Assigned to O I by chen.
2878·95 (2)	34724·8			8·77 (2)		
2876·30 (1*n*)	34756·7					
2836·34 (2)	35246·4					
2808·78 (2*n*)	35592·1			8·99 (1)		
2800·01 (1*n*)	35703·7					
2783·07 (1*n*)	35921·0			2·96 (1)		
2747·46 (6)	36386·52	$2s_1-3p_1$				} Isolated pair.
2733·34 (10)	36574·47	$2s_1-3p_2$		3·08 (4)		
2718·84 (2)	36769·5	$as'_1-bp'_1$		8·80 (1)		
2715·38 (3)	36816·4	$as'_1-bp'_2$		5·14 (2)		
2693·5 (0*n*)	37115					
2690·3 (0*n*)	37159					
2575·443 (1)	38816·65	$ap'_2-cd'_2$				} Isolated pair.
2575·300 (6)	38818·80	$ap'_2-cd'_3$		5·04 (3)		
2571·476 (4)	38876·54	$ap'_1-cd'_2$		1·31 (2)		
2530·30 (5)	39509·1			0·14 (2)		
2527·03 (1)	39560·2	$ap'_2-bp''_1$				
2526·89 (4)	39562·4	$ap'_2-bp''_2$		6·75 (2)		
2523·23 (3)	39619·8	$ap'_1-bp''_1$		2·98 (1)		XH 22·21 (1)
2523·09 (1)	39622·0	$ap'_1-bp''_2$				
2517·97 (4)	39702·6			7·80 (1)		
2445·55 (10)	40878·2	$2p_2-bd_3$		5·46 (4)		XH 45·47 (1), E 4
2444·26 (5)	40899·8	$2p_2-bd_2$		4·15 (3)		
2441·06 (1*n*)	40954·3					
2436·10 (4*n*)	41036·8			5·97 (2)		
2433·56 (9)	41079·6	$2p_1-bd_2$		3·52 (3)		XH 33·55 (1), E 3
2425·62 (5*n*)	41214·0			5·47 (2)		
2418·60 (1)	41333·7	$ad_3-cd'_2$				XH 18·62
2418·48 (6)	41335·7	$ad_3-cd'_3$		8·51 (3)		
2415·13 (3)	41393·0	$ap'_2-bs'_1$		5·02 (1)		
2411·64 (3*n*)	41452·9	$ap'_1-bs'_1$		1·52 (1)		
2407·49 (4)	41524·4	$ad_2-cd'_2$		7·38 (2)		
2407·37 (1)	41526·5	$ad_2-cd'_3$				
2406·41 (3*n*)	41543·0			6·29 (2)		
2375·73 (4)	42079·5	$ad_3-bp''_2$		5·64 (2)		
2365·15 (3)	42267·7	$ad_2-bp''_1$		5·07 (2)		
2365·03 (1)	42269·9	$ad_2-bp''_2$				
2339·38 (2)	42733·3			9·27 (1)		
2331·13 (*oo*)	42884·5					
2327·97 (2*n*)	42942·7			7·97 (1)		
2326·00 (1*n*)	42979·0			6·01 (1)		
2324·83 (*on*)	43000·7			4·83 (1)		
2322·14 (2*n*)	43050·5			2·13 (1)		

Table I—continued.

ensity.	ν.	Combinations.		Other Observations.		Remarks.
		Doublet.	Quartet.	Schneider-jost.	—	
66 ($4n$)	43096·5			9·64 (2)		
76 ($2n$)	43150·5			6·74 (1)		
10 ($3n$)	43162·7			6·13 (1)		
($2n$)	43219·5			3·08 (1)		
($1n$)	43319·5					
(5)	43411·6	$2p_2-bp'_1$		2·82 (1)		
(8)	43458·2	$2p_2-bp'_2$		0·35 (2)		
(6)	43591·5	$2p_1-bp'_1$		3·34 (2)		
(4)	43638·2	$2p_1-bp'_2$		0·82 (1)		
(3)	43752·5			4·71 (1)		This and following wave-lengths are provisional.
(2)	43779·3			3·43 (1)		
(1)	44179·3	ap'_2-4p_1				
(2)	44238·6	ap'_1-4p_1				
(3)	44373·4	ap'_2-4p_2		2·8 (1)		
(1)	44430·6	ap'_1-4p_2				
(2)	45529·3					
(1)	45613·2					
(2)	45634·0					
(1)	45657·9					
(0)	45724·7					
(4)	45799·9					
(0)	46246·4					
(0)	46270·6					
(0)	46529·4					
(5)	46888·3	$\begin{cases} ad_3-4p_2 \\ ad_2-4p_1 \end{cases}$				
(1)	47079·7	ad_2-4p_2				
(4)	47574·4	$ad_3-dd'_3$				
(0)	47599·1					
(2)	47765·3	$ad_2-dd'_2$				
(4)	48173·7					
(1)	48193·0					
(6)	48241·8					
(1)	49419·6					
1·45 (1)	49453·3					
0·44 (2)	49478·0					
0·27 (2)	49482·2					
6·60 (2)	49572·4					
3·61 (0)	50910·0					
3·20 (2)	50920·6					
1·60 (3)	50962·2					
9·70 (1)	51011·6					
6·78 (0)	51087·7					No additional lines of O II noted as far as λ 1850.

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* Lines of the group extending from λ 3048 to λ 2992 are extremely diffuse on most of the photographs. easurements in the first column are from a photograph taken at very low pressure ; lines of Si, C and O III have en eliminated as far as possible, and it is believed that the wave lengths tabulated correspond with the estimates the positions of the very diffuse lines indicated in the column of remarks.

§ The group λ 2915 to λ 2783 is similar in character to the group beginning at λ 3048.

Structure of the Spectrum.

In accordance with recent developments in the analysis of spectra, the spectrum of O I has been found to be built up from triplet and quintet terms. In a discussion of Hopfield's observations it has been shown by Laporte* that the supposed "doublet" system first traced by Runge and Paschen is in reality a triplet system, and is directly associated with the new set of triplets of short wave-lengths discovered by Hopfield; while the system previously supposed to consist of triplets is based upon quintet terms. From the position of oxygen in the periodic table, a septet system might also have been expected, but such terms have not yet been identified, and it seems possible that in elements of low atomic numbers lines depending upon the higher possible multiplicities are either weak or missing.

The spectrum of ionised oxygen (O II) was similarly expected to be built up from terms of doublet and quartet, and possibly sextet systems. Six pairs of lines having the separation $\Delta\nu = 179 \cdot 9$ noted by the present writer were the first evidence of a probable doublet system, and a quartet system of terms was first indicated by Paschen's observations of the Zeeman effect† in three lines of O II at λλ 3712·8, 3727·3, 3749·5. The work of Croze, to which reference has already been made, considerably elucidated the general structure of the spectrum by the identification of several doublet and quartet combinations. These results are included in the present paper, in some cases with further details resulting from the use of greater resolving power and more accurate measurements.

Notation.

In view of the lack of uniformity in spectroscopic notation, it is necessary to explain the system which has been adopted in the present paper. This is merely an adaptation of the generalised notation of Landé, in which the characteristics of a term are completely specified by n^r_{kj}, where k and j respectively represent the azimuthal and inner quantum numbers, and r is the maximum multiplicity in the group to which the term belongs. In practice n_k is replaced by a term symbol such as ms, mp, md, mf. . . ., it being understood that the values of k for s, p, d, f. . . . are 1, 2, 3, 4. . . . respectively. For a Rydberg sequence the individual terms are indicated by successive numerical values of m. Only one probable sequence, however, has yet been recognised in the spectrum of O II, and in other cases, when more than one term of the same type appears, the largest is designated by the prefix a, the second largest by b and so on. Terms of the same type are, of course, recognised as such by the structures of the multiplet combinations in which they appear, or by Zeeman effects.

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* 'Die Naturwissenschaften,' 12 Jahrg., Heft 29 (1924).

† Quoted by Landé, 'Zeit. f. Phys.,' vol. 15, p. 196 (1923).

The group multiplicity is indicated by an index on the upper left side of the term symbol; for example, a^2d (to be read as "a doublet d") denotes the largest d term identified in the doublet system, and b^4p (to be read as "b quartet p") the second largest in the quartet system.* The multiplicity figures, however, are omitted when there is no possibility of ambiguity.

The components of double or multiple terms are indicated in the usual way by subscripts on the right of the term symbols. In the present paper the subscripts adopted are the inner quantum numbers (j), as these would now appear to be more convenient than the older system, especially in connection with the higher multiplicities. Combinations are ordinarily restricted to those in which $\Delta j = \pm 1$ or 0, with the exclusion of the transition $0 \rightarrow 0$.

Besides the terms of ordinary types there are others which have been called "*gestrichene*," "primed" or "dashed" terms, and have been represented by $\bar{p}$, $\bar{d}$, ..., or p', d', ..., such terms being probably associated with the simultaneous displacement of two electrons. The form p', d', ... has been adopted in the present paper. Such terms are subject to the usual rules in regard to combinations among themselves, and the combinations show the same kinds of multiplets and the same Zeeman effects as those of corresponding ordinary terms. In their intercombinations with the ordinary terms, however, they follow the rule $\Delta k = 0$, and $\Delta k = \pm 1$ is forbidden; there is evidence also that the "primed" terms may combine with ordinary terms when $\Delta k = \pm 2$, as, for example, sd', the usual restrictions as to inner quantum numbers being observed.

In the spectra of the alkaline earths, Russell and Saunders† have found additional terms which generally combine in the same manner as terms of ordinary types, but differ from them in not forming part of the regular Rydberg series; for such terms they have suggested the use of doubly-accented letters, as p'', f''. In the spectrum of O II there are two terms which have been provisionally placed in this class, namely, ap'', bp''.

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* Compare Russell & Saunders, 'Astrophys. Journ.,' vol. 61, p. 66 (1925).

† *Loc. cit.*

Term Values.

The investigation of the structure of the spectrum was carried on in the first instance by adopting an arbitrary value for one of the terms of the doublet system, and another for a term of the quartet system. Afterwards, it appeared probable that three of the doublet p terms formed part of a Rydberg sequence, while two others could be considered to be of the p'' type as defined by Russell and Saunders. The three p terms in question are represented by the formula

$$mp_2 = 4\mathrm{R}/[m + 0\cdot316331 - 0\cdot310848/m]^2,$$

giving

$$2p_2 = 93952\cdot53$$
$$3p_2 = 42504\cdot63$$
$$4p_2 = 24419\cdot23$$

Although these values cannot yet be considered to be firmly established, they have been adopted in the tables for the doublet system which follow, and the remaining terms have been derived from the various combinations. These will at least serve the same purpose as values depending upon the assignment of an entirely arbitrary value to one of the terms.

In this connection it may be remarked that if the suggested Rydberg p sequence be justified, it seems possible that $1s$ will be found to be the largest term of the doublet system. The value of $1p_2$ indicated by the formula is 433942, which is quite improbably large for any term of the O II spectrum. On the other hand, the above values for $2p$ lead to 79078·69 for the term $2s$, and the corresponding value of $1s$ given by a simple Rydberg formula is 238,816. While this extrapolated term may be greatly in error, it represents an ionisation potential for O II of 29·5 volts, which is not hopelessly inconsistent with the 31 volts deduced from the discussion of stellar spectra.*

A further test of the proposed term values may be expected from observations in the extreme ultra-violet, particularly through the combination $1^2s - 2^2p$, but the available lists of oxygen lines in this region are not sufficiently detailed to provide a final test. It is, of course, possible that the deepest energy level may be represented by a term of the quartet system, but the quartet terms so far identified give no definite indications on this question.

[*Note added February* 5, 1926.—In a paper which has been published since the above was written (' Phil. Trans.,' A, vol. 225, p. 394) Mr. J. A. Carroll has quoted a list of oxygen lines measured by Bowen in the extreme ultra-violet, which includes two lines at λλ 625·84, 625·14 not previously resolved. The wave-numbers of these lines are 159785·2, 159964·2, and their separation, 179·0, is identical with that of the terms $2p_1$ and $2p_2$ within the limits of error. If these lines be taken as $1s—2p_1$ and $1s—2p_2$ of O II, the value of $1s$ becomes 253917, and would represent an ionisation potential of 31·35 volts, in close agreement with the astrophysical estimate.

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* R. H. Fowler and E. A. Milne, 'Monthly Notices R.A.S.,' vol. 84, p. 499 (1924); Miss C. Payne, 'Harvard Coll. Obs. Circ.,' No. 256 (1924).

Some doubt as to this interpretation, however, arises from the presence of another line at λ 624·61 (ν = 160099·9), which may possibly form a triplet with the two lines in question. If so, the three lines might be assignable to O III, for which Bowen and Millikan have already identified two triplets having somewhat similar separations. Details of these, using the wave-lengths quoted by Carroll, are as follows :

λ	ν	Δν	λ	ν	Δν
703·90	142065·6		508·23	196761·3	
		204·2			*186·0*
702·89	142269·8		507·75	196947·3	
		107·3			*116·4*
702·36	142377·1		507·45	197063·7	

The means of the separations are 195 and 112, as compared with 179 and 136 for the three lines under consideration. The discordance is larger than would be expected if the separations are really identical, as it is estimated that the wave-length separations may be relied upon to about 0·01 A (' Phil. Mag.,' vol. 48, p. 259, 1924). It does not seem possible to reach a final decision, however, until the measurements have been checked, or the structure of the O III spectrum has been more fully investigated.]

As no intercombinations between the doublet and quartet systems have been identified, the tabulated terms of the quartet system are entirely based upon an assumed value of 100,000 for the a^4p_3 term. It will be understood that while the stated values of the terms themselves may be grossly in error, their differences are exact within the limits of error of the observations.

THE DOUBLET SYSTEM.

The terms of the doublet system which have so far been traced are collected in Table II, it being understood that the values stated have been reached on the supposition that three of the p terms form an ordinary sequence, having 4 R for the series constant. The adopted values of some of the terms have been derived from measurements of a high order of accuracy ; otherwise, the values are the means of the determinations from the various combinations into which they enter. The general accuracy of the measurements throughout is indicated by the close agreement between the observed wave-numbers of the lines and those obtained from differences of the corresponding terms.

Table II.—Terms of the Doublet System.

		Δν			Δν
$1\,s_1$	[238,816]*		as'_1	87310·5	
$2\,s_1$	79078·69		bs'_1	27398·5	
$2\,p_1$	94132·52	*179·99*	ap'_1	68851·16	*59·74*
$2\,p_2$	93952·53		ap'_2	68791·42	
$3\,p_1$	42692·15	*187·53*	bp'_1	50540·8	*46·6*
$3\,p_2$	42504·62		bp'_2	50494·2	
$4\,p_1$	24612·3	*193·1*			
$4\,p_2$	24419·2		†ad'_3	76049·6	*1·0*
			ad'_2	76048·6	
†ap''_2	49590·80	*113·99*	bd'_2	48618·42	*51·97*
ap''_1	49476·81		bd'_3	48565·45	
bp''_1	29231·39	*2·36*	cd'_2	29974·67	*2·12*
bp''_2	29229·03		cd'_3	29972·55	
			†dd'_3	23734·7	*0·8*
ad_2	71498·92	*190·68*	dd'_2	23733·9	
ad_3	71308·24				
†bd_3	53074·3	*21·6*			
bd_2	53052·7				

* Extrapolated from 2 *s*.
† Inverted terms ; *i.e.*, $p_2 > p_1$, or $d_3 > d_2$.

The combinations of doublet terms are shown in Table III.

It should be remarked that lines corresponding to some of the expected combinations fall outside the range of the present observations and consequently do not appear in the tables. There is, however, a notable exception in the combination $a\,d - a\,p''$, which might have been expected to appear in the blue part of the visible spectrum. No trace of this has been found, and its absence may be in some way associated with the fact that the $a\,p''$ terms are inverted (*i.e.*, $a\,p_2 > a\,p_1$), suggesting a further restricting condition in the combination of terms. The apparent absence of lines corresponding to other combinations which are theoretically possible may generally be attributed to their feeble intensities, since the smaller terms are involved.

In all cases the terms are arranged in increasing order from left to right, and in decreasing order of magnitude downwards in each group of combinations of terms of similar type.

Wave numbers which are enclosed in brackets have been calculated from the respective terms.

Table III.—Doublet Combinations.

$^2s\ ^2p$ *Combinations.*

$2s_1 = 79078\cdot69$

	$\Delta\nu$.	
$2p_2 - 2s_1 = 14873\cdot87$ (5)	*180·18*	$2p_2 = 93952\cdot53$
$2p_1 - 2s_1 = 15054\cdot05$ (4)		$2p_1 = 94132\cdot52$
$2s_1 - 3p_1 = 36386\cdot52$ (6)	*187·95*	$3p_1 = 42692\cdot15$
$2s_1 - 3p_2 = 36574\cdot47$(10)		$3p_2 = 42504\cdot62$
$2s_1 - ap''_2 = 29487\cdot92$ (8)	*113·94*	$ap''_2 = 49590\cdot80$
$2s_1 - ap''_1 = 29601\cdot86$ (7)		$ap''_1 = 49476\cdot81$

$^2d\ ^2p$ *and* $^2d\ ^2p''$ *Combinations.*

Term Values.	ad_3 71308·24	*190·68*	ad_2 71498·92	Combinations.
$2p_1 = 94132\cdot52$			22633·60(8)	$2p - ad$
179·99			*179·98*	
$2p_2 = 93952\cdot53$	22644·29(10)	*190·67*	22453·62(6)	
$3p_1 = 42692\cdot15$			28806·74(5)	$ad - 3p$
187·53			*187·47*	
$3p_2 = 42504\cdot62$	28803·50(8)	*190·71*	28994·21(5)	
$4p_1 = 24612\cdot3$			*46888·3(5)	$ad - 4p$
193·1				
$4p_2 = 24419\cdot2$	*46888·3(5)		47079·7(1)	
$bp''_1 = 29231\cdot39$			42267·7(3)	$ad - bp''$
2·36			*2·2*	
$bp''_2 = 29229\cdot03$	42079·5(4)	*190·4*	42269·9(1)	
	bd_3 53052·7	*21·6*	bd_2 53074·3	
$2p_1 = 94132\cdot52$	41079·6(9)			$2p - bd$
179·99	*179·8*			
$2p_2 = 93952\cdot53$	40899·8(5)	*21·6*	40878·2(10)	
$bp''_1 = 29231\cdot39$	23821·44(1)			$bd - bp''$
2·36	[*2·4*]			
$bp''_2 = 29229\cdot03$	[23823·8]	[*21·6*]	23845·42(2)	

* Not resolved.

$^2s'\ ^2p'$ *Combinations.*

$as'_1 = 87310\cdot5$ $bs'_1 = 27398\cdot5$

$as'_1 - bp'_1 = 36769\cdot5$(2)	*46·9*	$bp'_1 = 50540\cdot8$
$as'_1 - bp'_2 = 36816\cdot4$(3)		$bp'_2 = 50494\cdot2$
$bp'_2 - bs'_1 = 23095\cdot58$(2)	*46·46*	
$bp'_1 - bs'_1 = 23142\cdot04$(1)		
$ap'_2 - bs'_1 = 41393\cdot0$(3)	*59·9*	$ap'_2 = 68791\cdot42$
$ap'_1 - bs'_1 = 41452\cdot9$(3)		$ap'_1 = 68851\cdot16$

Table III—continued.

${}^2p'\,{}^2d'$ *Combinations.*

Term Values.	ap'_2 68791·42	*59·74*	ap'_1 68851·16	Combinations.
bd'_2 = 48618·42	20172·84 (3)	*59·86*	20232·70 (5)	$ap' - bd'$
51·97	*51·92*			
bd'_3 = 48565·45	20224·76 (7)			
cd'_2 = 29974·67	38816·65 (1)	*59·89*	38876·54 (4)	$ap' - cd'$
2·12	*2·15*			
cd'_3 = 29972·55	38818·80 (6)			
dd'_3 = 23734·7	45056·8 (2)			$ap' - dd'$
0·8	[*0·8*]			
dd'_2 = 23733·9	[45057·6]	[*59·8*]	45117·4 (1)	
	bp'_2 50494·2	*46·6*	bp'_1 50540·8	
ad'_3 = 76049·6	25555·48 (10)			$ad' - bp'$
1·0	*0·89*			
ad'_2 = 76048·6	25554·59 (2)	*46·89*	25507·70 (6)	
cd_2 = 29974·67	[20519·44]	*46·60*	20566·04 (3)	$bp' - cd'$
2·12	[*2·06*]			
cd'_3 = 29972·55	20521·50 (5)			
dd'_3 = 23734·7	26759·43 (3)			$bp' - dd'$
0·8	[*0·8*]			
dd'_2 = 23733·9	[26760·2]	[*46·6*]	26806·78 (2)	

${}^2p\,{}^2p'$ *and* ${}^2p'\,{}^2p''$ *Combinations.*

Term Values.	ap'_2 68791·42	*59·74*	ap'_2 68851·16	Combinations.
$2p_1$ = 94132·52	25341·10 (5)	*59·74*	25281·36 (7)	$2p - ap'$
179·99	*179·98*		*179·99*	
$2p_2$ = 93952·53	25161·12 (10)	*59·75*	25101·37 (5)	
$3p_1$ = 42692·15	26099·22 (4*r*)	*59·88*	26159·10 (4*r*)	$ap' - 3p$
187·53	*187·41*		*187·42*	
$3p_2$ = 42504·62	26286·63 (6*r*)	*59·89*	26346·52 (3*r*)	
$4p_1$ = 24612·3	44179·3 (1)	*59·3*	44238·6 (2)	$ap' - 4p$*
193·1	*194·1*		*192·0*	
$4p_2$ = 24419·2	44373·4 (3)	*57·2*	44430·6 (1)	
ap''_2 = 49590·80	19200·58 (5)	*59·82*	19260·40 (3)	$ap' - ap''$
113·99	*113·99*		*113·99*	
ap''_1 = 49476·81	19314·57 (2)	*59·82*	19374·39 (4)	
bp''_1 = 29231·39	39560·2 (1)	*59·6*	39619·8 (3)	$ap' - bp''$
2·36	*2·2*		*2·2*	
bp''_2 = 29229·03	39562·4 (4)	*59·6*	39622·0 (1)	

* Provisional wave-numbers.

Table III—continued.

$^2p\,^2p'$ *and* $^2p'\,^2p''$ *Combinations*—continued.

	bp'_2 50494·2	*46·6*	bp'_1 50540·8	Combinations.
$2p_1$ = 94132·52	43638·2 (4)	*46·7*	43591·5 (6)	$2p - bp'$
179·99	*180·0*		*179·9*	
$2p_2$ = 93952·53	43458·2 (8)	*46·6*	43411·6 (5)	
bp''_1 = 29231·39	21262·70 (0)	*46·63*	21309·33 (1)	$bp' - bp''$
2·36	*2·40*		*2·27*	
bp''_2 = 29229·03	21265·10 (2)	*46·50*	21311·60 (0)	

$^2d\,^2d'$ *Combinations.*

Term Values.	ad_3 71308·24	*190·68*	ad_2 71498·92	Combinations.
bd'_2 = 48618·42	22689·86 (1)	*190·80*	22880·66 (4)	$ad - bd'$
51·97	*51·98*		*51·96*	
bd'_3 = 48565·45	22741·84 (7)	*190·78*	22932·62 (1)	
cd'_2 = 29974·67	41333·7 (1)	*190·7*	41524·4 (4)	$ad - cd'$
2·12	*2·0*		*2·1*	
cd'_3 = 29972·55	41335·7 (6)	*190·4*	41526·5 (1)	
dd'_3 = 23734·7	47574·4 (4)		—	$ad - dd'$
0·8				
dd'_2 = 23733·9	—		47765·3 (2)	
	bd_2 53052·7	*21·6*	bd_3 53074·3	
ad'_3 = 76049·6	[22996·9]		22975·33 (6)	$ad' - bd$
1·0				
ad'_2 = 76048·6	22995·66 (5)	[*21·6*]	[22974·3]	
cd'_2 = 29974·67	23078·15 (2)	*21·32*	23099·47 (0)	$bd - cd'$
2·12	*2·23*		*2·19*	
cd'_3 = 29972·55	23080·38 (0)	*21·26*	23101·66 (3)	
dd'_3 = 23734·7	[29318·0]		29339·68 (7n)	
0·8				
dd'_2 = 23733·9	29318·50 (6n)		[29340·4]	

Attention should also be directed to the following lines of somewhat doubtful classification :—

Term Values.	ad_3 71308·24	*190·68*	ad_2 71498·92	Combinations.
xd'_3 = 92582·48	21274·23 (7)	*190·67*	21083·56 (3)	$xd' - ad$
	48·92		*48·75*	
xd'_2 = 92533·64	21225·31 (5)	*190·50*	21034·81 (2)	

In view of the fact that 21,034 is too weak for its classification, and that no other expected combinations have been found, this multiplet remains doubtful.

Among others, the following important pairs are not included in the foregoing scheme of doublets :—

λ		ν	Δν
4596·189	(8)	21751·08	*24·68*
4590·983	(9)	21775·76	
4189·793	(10)	23860·82	*24·75*
4185·453	(8)	23885·57	
2530·30	(5)	39509·1	*193·5* = $\Delta 4^2 p$?
2517·97	(4)	39702·6	

THE QUARTET SYSTEM.

The relative magnitudes of the terms of the quartet system which have hitherto been identified are collected in Table IV, a value of 100,000 having been adopted for the a^4p_3 term. Of the ordinary class of terms—one is of s type, two of p, one of d and one of f type. One term is of p' and one of d' type. One term, having 3 for its inner quantum number, of which the type is not yet clear, has been designated x_3.

Table IV.—Terms of the Quartet System.

Ordinary Terms.		Δν	Primed Terms.		Δν
s_2	= 73337·26				
ap_1	= 100263·84	*105·32*	p'^1	= 77153·03	*46·10*
ap_2	= 100158·52	*158·52*	p'_2	= 77106·93	*91·97*
ap_3	= 100,000·00		p'_3	= 77014·96	
bp_1	= 46872·88	*105·22*			
bp_2	= 46767·66	*161·42*			
bp_3	= 46606·24				
d_1	= 78768·40	*55·54*	d'_1	= 52753·69	*0·47*
d_2	= 78712·86	*91·56*	d'_2	= 52753·22	*1·53*
d_3	= 78621·30	*124·62*	d'_3	= 52751·69	*6·35*
d_4	= 78496·68		d'_4	= 52745·34	
f_2	= 54203·15	*54·03*			
f_3	= 54149·12	*77·91*			
f_4	= 54071·21	*102·27*			
f_5	= 53968·94				

$x_3 = 52702·93$

Combinations of the quartet terms are indicated in Table V, which is in the same form as Table III.

Table V.—Quartet Combinations.

$^4s\,^4p$ *Combinations.*

s_2 = 73337·26

	Δν	
$ap_3 - s_2$ = 26662·74 (9)		ap_3 = 100000·00
	158·52	
$ap_2 - s_2$ = 26821·26 (8)		ap_2 = 100158·52
	105·32	
$ap_1 - s_2$ = 26926·58 (7)		ap_1 = 100263·84
$s_2 - bp_1$ = 26464·35 (4*r*)		bp_1 = 46872·88
	105·28	
$s_2 - bp_2$ = 26569·63 (5*r*)		bp_2 = 46767·66
	161·35	
$s_2 - bp_3$ = 26730·98 (6*r*)		bp_3 = 46606·24

$^4d\,^4p$ *and* $^4d\,^4f$ *Combinations.*

Term Values.	d_4 78496·68		d_3 78621·30		d_2 78712·86		d_1 78768·40
		124·62		*91·56*		*55·54*	
p_1 = 100263·84					21550·98(6)	*55·55*	21495·43(6)
105·32					*105·34*		*105·31*
p_2 = 100158·52			21537·23(9)	*91·59*	21445·64(9)	*55·52*	21390·12(4)
158·52			*158·53*		*158·49*		
p_3 = 100000·00	21503·32(10)	*124·62*	21378·70(8)	*91·55*	21287·15(2)		(*ap* − *d*)
p_1 = 46872·88					31840·27(4*r*)	*55·37*	31895·64(3*r*)
105·22					*105·10*		*105·18*
p_2 = 46767·66			31853·78(8*r*)	*91·59*	31945·37(7*r*)	*55·45*	32000·82(2*r*)
161·42			*161·36*		*161·38*		
p_3 = 46606·24	31890·56(10*r*)	*124·58*	32015·14(6*r*)	*91·61*	32106·75(1*r*)		(*ad* − *bp*)
= 54203·15			24418·05(0)	*91·69*	24509·74(4)	*55·57*	24565·31(4)
54·03			*54·15*		*53·96*		
= 54149·12	24347·57(0)	*124·63*	24472·20(3)	*91·50*	24563·70(6)		
77·91	*77·88*		*77·91*				
= 54071·21	24425·45(5)	*124·66*	24550·11(8)				
102·27	*102·29*						
= 53968·94	24527·74(10)						(*d* − *f*)

$^4p\,^4p'$ *Combinations.*

Term Values.	p'_3 77014·96		p'_2 77106·93		p'_1 77153·03	Combinations.
		91·97		*46·10*		
ap_1 = 100263·84			23156·88 (8)	*46·08*	23110·80 (3)	
105·32			*105·18*		*105·30*	
ap_2 = 100158·52	23143·55 (8)	*91·85*	23051·70 (6)	*46·20*	23005·50 (7)	*ap* − *p*′
158·52	*158·50*		*158·61*			
ap_3 = 100000·00	22985·05 (8)	*91·96*	22893·09 (7)			
bp_1 = 46872·88			30233·87 (6*r*)	*46·16*	30280·03 (3*r*)	
105·22			*105·25*		*105·19*	
bp_2 = 46767·66	30247·13 (6*r*)	*91·99*	30339·12 (4*r*)	*46·10*	30385·22 (5*r*)	*p*′ − *bp*
161·42	*161·55*		*161·41*			
bp_3 = 46606·24	30408·68 (9*r*)	*91·85*	30500·53 (7*r*)			

Table V—continued.

$^4d'\ ^4p'$ and $^4d'\ ^4d$ Combinations.

Term Values.	d'_4 52745·34	*6·35*	d'_3 52751·69	*1·53*	d'_2 52753·22	*0·47*	d'_1 52753·69
p'_1 = 77153·03					24399·76 (4)	*0·42*	24399·34 (1)
46·10					*46·08*		
p'_2 = 77106·93			24355·24 (5)	*1·56*	24353·68 (7)		[24353·26]
91·97			*91·99*		*91·90*		
p'_3 = 77014·96	24269·61 (8)	*6·36*	24263·25 (3)	*1·47*	24261·78 (2)		$(p' - d')$
d_1 = 78768·40					26015·20 (3)		[26014·71]
55·54					*55·51*		
d_2 = 78712·86			25961·22 (2)	*1·53*	25959·69 (3)		[25959·17]
91·56			*91·63*		*91·63*		
d_3 = 78621·30	25875·96 (2)	*6·37*	25869·59 (5)	*1·53*	25868·06 (1)		
124·62	*124·59*		*124·57*				
d_4 = 78496·68	25751·37 (7)	*6·35*	25745·02 (3)				

$x\ ^4d$, $x\ ^4p'$ and $x\ ^4s$ Combinations.

$x_3 = 52702·93$

	$\Delta\nu$	
$d_4 - x_3 = 25793·70$ (4)		$d_4 = 78496·68$
	124·65	
$d_3 - x_3 = 25918·35$ (4)		$d_3 = 78621·30$
	91·70	
$d_2 - x_3 = 26010·05$ (3)		$d_2 = 78712·86$
$p'_3 - x_3 = 24312·00$ (4)		$p'_3 = 77014·96$
	91·98	
$p'_2 - x_3 = 24403·98$ (3)		$p'_2 = 77106·93$
$s_2 - x_3 = 20634·04$ (1)		$s_2 = 73337·26$

The value of j_x which satisfies the above combinations is clearly 3, but the character of the x term remains uncertain; it may be an unresolved ^4p or $^4d'$ term, or possibly a term of the sextet system.

The combination $^4s\ ^4d'$ also occurs, as will appear from the following:

Calculated	Observed.
$s_2 - d'_1 = 20583·57$ $s_2 - d'_2 = 20584·03$	20583·88 (3)
$s_2 - d'_3 = 20585·56$	20585·27 (2)

The following lines involving already recognised $\Delta\nu$ may also be noted:

23277·34 (3)		23978·50 (4)	
	105·06		*91·92*
23382·40 (4)		24070·42 (7)	
			55·42
		24125·84 (2)	

COMPARISON OF O II AND N I.

The atomic number of oxygen being 8 and that of nitrogen 7, it is to be expected that the spectrum of singly-ionised oxygen (O II) will be of a similar character to that of neutral nitrogen (N I). The lines of O II, however, will be of higher frequencies than corresponding lines of N I in consequence of the greater charge of the "atomic residue," or "core," with respect to the emitting electron, and separations in corresponding pairs or groups may be expected to be larger in O II than in N I.

The spectrum of N I has recently become more completely known through the experiments of Merton and Pilley,* and a preliminary analysis of the spectrum has been made by C. C. Kiess.† It results that the spectrum is built up from doublet and quartet terms, the largest identified term of each system being of *p* type. Although it is not yet possible to make an extensive comparison of the two spectra, it will be of interest to compare some of the probably corresponding terms and combinations. The doublets of N I not yet having been worked out in sufficient detail for effective comparison with O II, attention will be confined to the quartet systems.

Among the quartet combinations which may be compared are the following *sp* groups, the notation being that adopted for O II in the present communication.

	O II		N I		O II/N I
$a\,{}^4p_3 - {}^4s_2$	26662·74	(9)	13385·47	(5)	1·992
$a\,{}^4p_2 - {}^4s_2$	26821·26	(8)	13432·54	(4)	1·997
$a\,{}^4p_1 - {}^4s_2$	26926·58	(7)	13466·34	(3)	2·000
	$\Delta\,ap_{32}$	$\Delta\,ap_{21}$	$\Delta\,ap_{32}$	$\Delta\,ap_{21}$	
	158·52	*105·32*	*47·07*	*33·80*	
Ratio Observed	4·5 :	3	4·2 :	3	
Ratio Calculated	5 :	3	5 :	3	
${}^4s_2 - b\,{}^4p_1$	26464·35	(4)	13061·73		2·026
${}^4s_2 - b\,{}^4p_2$	26569·63	(5)	13106·07		2·027
${}^4s_2 - b\,{}^4p_3$	26730·98	(6)	13176·19		2·029
	$\Delta\,bp_{32}$	$\Delta\,bp_{21}$	$\Delta\,bp_{32}$	$\Delta\,bp_{21}$	
	161·35	*105·28*	*70·12*	*44·34*	
Ratio Observed	4·6 :	3	4·7 :	3	
Ratio Calculated	5 :	3	5 :	3	

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* 'Roy. Soc. Proc.,' A, vol. 107, p. 411 (1925).

† 'Journ. Opt. Soc. America,' vol. 11, p. 1 (1925).

The correspondence for these two triplets is very close. In each spectrum the stronger triplet has the larger separation towards the red, whilst the weaker one has the larger separation towards the violet. In O II the two triplets slightly overlap, whilst in N I they are a little separated. The ratios of the separations are nearly the same in both and approximate to Landé's calculated separations of 5 : 3 for ^4p terms. It will also be observed that the wave-numbers in O II are almost exactly double those in N I. The ratios of the separations of the O II to those of the N I triplets, however, are not nearly so constant, being more than 3 : 1 for the first, and about 2·4 : 1 for the second triplet.

Other corresponding quartet combinations, which it is unnecessary to exhibit in full detail, are the following :—

	O II	N I	O II/N I
$a\,^4p_3 - {}^4d_4$	21503·32(10)	11517·11(3)	1·867
$^4d_4 - b^4p_3$	31890·56(10)	15044·84(7)	2·120

	Δd_{43}	Δd_{32}	Δd_{21}	Δd_{43}	Δd_{32}	Δd_{21}
	124·62	*91·56*	*55·54*	*50·98*	*37·35*	*22·59*
Ratio Observed	6·81	: 5·00	: 3·03	6·82	: 5·00	: 3·02
Ratio Calculated	7	: 5	: 3	7	: 5	: 3

	O II	N I	O II/N I
$a\,^4p_3 - {}^4p'_3$	22985·05(8)	12167·36(5)	1·889
$^4p'_3 - b^4p_3$	30408·68(9)	14394·51(3)	2·112

	$\Delta p'_{32}$	$\Delta p'_{21}$	$\Delta p'_{32}$	$\Delta p'_{21}$
	91·97	*46·10*	*38·36*	*18·38*
Ratio Observed	6·0	: 3	6·3	: 3
Ratio Calculated	5	: 3	5	: 3

In all these the wave-numbers of the O II are again roughly double those of the corresponding N I combinations, and the term separations are nearly in the same ratios in the two spectra, though in varying discordance with Landé's rules. The ratios of the term separations of O II to those of N I range from 2·4 to 2·5, and are not very different from those in the second *sp* triplet mentioned above.

Only one $^4d\,^4f$ multiplet has been identified in each spectrum, namely :—

	O II	N I	O II/N I
$^4d_4 - {}^4f_5$	24527·74(10)	15421·32(9)	1·59

	Δf_{54}	Δf_{43}	Δf_{32}	Δf_{54}	Δf_{43}	Δf_{32}
	102·27	*77·91*	*54·03*	*56·06*	*34·70*	*17·74*
Ratio Observed	9·19	: 7·00	: 4·85	11·31	: 7·00	: 3·58
Ratio Calculated	9	: 7	: 5	9	: 7	: 5

In these combinations the wave-number of the leading line of the O II group is much less than double that of the corresponding N I line. Further, although in O II the separation ratios are in close accordance with Landé's rule, those of the N I group are more nearly in the relation 3 : 2 : 1 than 9 : 7 : 5. The total separations, Δf_{52}, however, are in the ratio 2·2 : 1, and in this respect approximate to the ratios of most of the other term separations.

The outcome of the comparison is to suggest a close similarity between the spectra of O II and N I, most of the quartet groups of lines in O II having wave-numbers which are approximately double those of corresponding groups of N I. Apart from the a^4p and ^4f terms, the ratios of the corresponding term separations in O II and N I are nearly constant, and not far from 2·4 : 1.

Summary.

The spectrum of oxygen in the region λ 6750–λ 1850 has been investigated under different conditions, and many previously unrecorded lines have been measured. In the present communication, particulars are given of about 400 lines, which are attributed to the singly-ionised atom (O II). The structure of this spectrum has been further elucidated, 90 lines having been assigned to the doublet system and 68 to the quartet system.

On the supposition that three of the doublet p terms form a Rydberg sequence, with 4 R for the series constant, the value 93952 has been assigned to the term $2\ ^2p_2$, and the values of other terms have been deduced from the various combinations. The term 2 s thus derived suggests about 240,000 for the 1 s term, and if this represents the deepest energy level, the corresponding value for the ionisation potential will be about 30 volts, in fair accordance with the 31 volts deduced from stellar spectra. As the calculated $1\,s - 2\,p$ lines lie in the extreme ultra-violet, and have not yet been identified, this result cannot be regarded as final.

As no intercombinations between the doublets and quartets have been traced, the tabulated quartet terms depend upon an arbitrary value assigned to one of them.

So far as a comparison can at present be made, the spectra of O II and N I, as expected, show a close similarity, the wave-numbers of several of the groups of lines in O II being approximately double those of the corresponding groups of N I.

The author has pleasure in acknowledging the effective help which has been given by Mr. E. W. H. Selwyn, B.Sc., in connection with the experimental work which forms the basis of the foregoing paper.

The Spectrum of Ionised Nitrogen (N II).

By A. Fowler, F.R.S., Yarrow Research Professor of the Royal Society, and L. J. Freeman, B.Sc., D.I.C., Imperial College of Science and Technology, South Kensington.

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[Plates 47, 48.]

Introductory.

In a previous communication* it was shown that many of the lines in the spectrum of singly-ionised nitrogen (N II) in the region λ 6000 to λ 3000 were accounted for by triplet and singlet terms, in agreement with theoretical expectation. The observational data have since been extended over a much greater range, and the purpose of the present paper is to give the results of a more complete analysis of the spectrum, together with a list of all the lines which are considered to be due to N II.

The further analysis of the spectrum has been facilitated by the recent developments of the theory of spectra which we owe to Pauli, Heisenberg and Hund.† The theory enables the types of spectroscopic terms associated with any specified configuration of the electrons to be predicted, besides indicating the terms which may, or may not, combine with each other, and terms which may be properly associated in the same Rydberg sequence. Thus, as pointed out by Laporte,‡ although the two terms of "p" type indicated in the previous paper belong to a Rydberg sequence, one of them is theoretically the deepest possible term of this type, so that extrapolation for the evaluation of a deeper term of the same sequence is not permissible; on the other hand, the theory indicates that the deepest term of the spectrum, in the notation of the previous paper, is of the p' type, and the extrapolated value from the observed term of this type appeared to be in general agreement with that deduced from astrophysical considerations. It thus appears that the approximate value of 70,000 previously assigned to the first p term should have been assigned to the p' term, and that all the term values were consequently too low by about 20,000 units of wave-number.

The majority of the brighter lines, and many of the fainter ones, have now been classified, and most of them have been found to be derived from terms predicted for transitions of a single electron. There are, however, a few definite groups of lines which are not accounted for by this set of terms, and it would seem that these must arise from simultaneous transitions of two of the valence electrons.

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* A. Fowler, 'Roy. Soc. Proc.,' A, vol. 107, p. 31 (1924).

† 'Z. f. Physik,' vol. 33, p. 345 (1925). See also R. H. Fowler and D. R. Hartree, 'Roy. Soc. Proc.,' A, vol. 111, p. 83 (1926), and McLennan, McLay & Smith, 'Roy. Soc. Proc.,' A, vol. 112, p. 76 (1926).

‡ 'Jour. Opt. Soc., America,' vol. 13, p. 13 (1926).

Observational Data.

The spectrum has been investigated mainly by the use of condensed discharges in vacuum tubes containing nitrogen at various pressures. Under these conditions, the spectrum of neutral atoms of nitrogen (N I) is represented only by the two well-known pairs of lines in the Schumann region at wave-lengths 1745·3, 1742·7, 1494·8, 1492·8, from which it may be inferred that most of the nitrogen molecules break down directly into ionised atoms. With discharges of moderate intensity, the N II spectrum thus appears almost alone, but stronger discharges result in the appearance of lines of N III, N IV, and even of N V.* From a comparison of the spectra obtained with different discharges and pressures, it was not difficult to separate lines of N II from those representing higher stages of ionisation, even in the region of short wave-lengths beyond the transmission of fluorite. An attempt has been made to record all the lines of N II, faint as well as strong, in the region extending from λ 6850 in the red to λ 830, which appears to be the limit of action of the vacuum spectrograph, at present available. Lines of nitrogen of still shorter wave-lengths, however, have been recorded in the "hot spark" spectrum by Millikan and his colleagues.

The positions of many of the brighter lines from λ 5045 to λ 3919 have been determined in the third order of a 10-ft. concave grating, and are distinguished in the general catalogue (Table I) by their being stated to three decimal places. The remaining lines, except the fainter ones in the green, yellow and red, were measured on photographs taken in the first order of the grating (5·6 Å per mm.), or with glass and quartz spectrographs of the same order of dispersion, or greater, and are not expected to be in error by more than two or three hundredths of an Ångström. As mentioned in the previous paper, however, there are some lines which are subject to displacements at higher pressures of the gas in vacuum tubes, and although photographs of the spectrum at low pressures have been chiefly measured, it is not certain that such displacements have been altogether eliminated. Wave-lengths between λ 1850 and λ 1215 were measured on photographs taken in the first order of the Hilger vacuum spectrograph, having a concave grating of 1 metre radius and giving a dispersion of about 17 Å per millimetre ; from λ 1215 to λ 830 the second order was used. Carbon sparks in nitrogen at atmospheric pressure, with varying amounts of self-induction, provided a useful additional source within the range of transmission of a fluorite window. Good standards for wave-length determinations are now provided by Lang and Smith's very accurate measures of carbon lines,* and by measures of carbon, oxygen and nitrogen lines which have been made by Bowen and Ingram.†

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* The pair of lines at λλ 1242·93, 1238·94, attributed to N V by Millikan and Bowen, has been obtained strongly in the vacuum discharge, and also with less intensity in the condensed spark in nitrogen at atmospheric pressure.

The intensities of the lines are indicated throughout by numbers in brackets following the wave-lengths or wave-numbers. Such estimates give a fair indication of the relative intensities over a short range of the spectrum, and especially in individual multiplets, but do not necessarily show the relative intensities of lines in widely separated regions. Wave-numbers have been calculated from the wave -lengths with the aid of the convenient tables published by Kayser.‡

Details of the wave-lengths, intensities, wave-numbers and classification of the N II lines are collected in Table I. Wave-lengths greater than λ 1850 are the values *in air*, while shorter wave-lengths are *in vacuo*, λ 1850 being near the limit for quartz spectrographs.

Table I.—N II Lines, λ 6850 — λ 915.

λ, Intensity.	ν.	Classification.
6836·2 (1)	14624·0	$1\,{}^3P_1'''-2\,{}^3S_1'$
6812·26 (2)	14675·4	$1\,{}^3P_2'''-2\,{}^3S_1'$
6630·5 (2)	15077·7	
6610·58 (6)	15123·06	
[6554·7]	[15252]	$1\,{}^3D_2-2\,{}^3D_1'$
6545·2 (0)	15274·2	$\left\{\begin{array}{l}1\,{}^3D_3-2\,{}^3D_2'\\1\,{}^3D_1-2\,{}^3D_1'\end{array}\right.$
6533·0 (1)	15302·7	$1\,{}^3D_2-2\,{}^3D_2'$
6522·3 (0)	15327·8	$1\,{}^3D_1-2\,{}^3D_2'$
6515·2 (0)	15344·5	
6504·9 (2)	15368·8	$1\,{}^3D_3-2\,{}^3D_3'$
6492·0 (0)	15399·3	$1\,{}^3D_2-2\,{}^3D_3'$
6482·07 (8)	15422·92	$1\,{}^1P_1'-2\,{}^1D_2'$
6379·63 (5)	15670·57	$1\,{}^3P_1'-2\,{}^1D_2'$
6365·7 (0)	15704·9	
6357·0 (3)	15726·4	
6347·1 (1)	15750·9	
6340·67 (4)	15766·85	
6328·6 (1)	15796·9	
6284·30 (3)	15908·28	$1\,{}^1P_1-1\,{}^1P_1'''$
6242·52 (5)	16014·75	
6173·40 (3)	16194·06	$1\,{}^3F_3'-2\,{}^3D_2'$
6170·16 (1)	16202·56	$1\,{}^3F_2'-2\,{}^3D_1'$
6167·82 (4)	16208·71	$1\,{}^3F_4'-2\,{}^3D_3'$
6150·9 (0)	16253·3	$1\,{}^3F_2'-2\,{}^3D_2'$
6136·9 (0)	16290·4	$1\,{}^3F_3'-2\,{}^3D_3'$
6114·6 (0)	16349·8	$1\,{}^3F_2'-2\,{}^3D_3'$
6065·5 (0)	16484·8	
5960·93 (0)	16771·27	$2\,{}^3P_2-1\,{}^3D_1$
5952·39 (3)	16795·33	$2\,{}^3P_2-1\,{}^3D_2$
5941·67 (8)	16825·63	$2\,{}^3P_2-1\,{}^3D_3$
5940·25 (2)	16829·66	$2\,{}^3P_1-1\,{}^3D_1$
5931·79 (7)	16853·66	$2\,{}^3P_1-1\,{}^3D_2$
5927·82 (4)	16864·95	$2\,{}^3P_0-1\,{}^3D_1$

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* 'Phys. Rev.,' vol. 28, p. 36 (1926).

† 'Phys. Rev.,' vol. 28, p. 444 (1926).

‡ 'Tabelle der Schwingungzahlen,' Leipzig (1925).

Table I—(continued).

ntensity.	ν.	Classification.
·43 (3)	17333·95	$1\,{}^1P_1'-1\,{}^3D_1'$
·29 (4)	17394·69	$1\,P_1'-1\,{}^3D_2'$
·67 (2)	17445·14	$1\,{}^3P_2'-1\,{}^3D_1'$
·76 (6)	17505·96	$1\,{}^3P_2'-1\,{}^3D_2'$
·21 (6)	17581·54	$1\,{}^3P_1'-1\,{}^3D_1'$
·56 (10)	17602·12	$1\,{}^3P_2'-1\,{}^3D_3'$
·02 (6)	17613·10	$1\,{}^3P_0'-1\,{}^3D_1'$
·64 (8)	17642·26	$1\,{}^3P_1'-1\,{}^3D_2'$
·30 (0)	17963·51	$a\,{}^3P_2'-a\,{}^3D_1'$
·95 (3)	18006·70	$a\,{}^3P_2'-a\,{}^3D_2'$
·49 (3)	18034·18	$a\,{}^3P_1'-a\,{}^3D_1'$
·16 (1)	18045·02	
·39 (5)	18060·57	$a\,{}^3P_2'-a\,{}^3D_3'$
·27 (4)	18077·29	$a\,{}^3P_1'-a\,{}^3D_2'$
·26 (2)	18090·41	$a\,{}^3P_0'-a\,{}^3D_1'$
·70 (5)	18191·00	$2\,{}^3P_2-1\,{}^3P_2'''$
·10 (3)	18242·79	$2\,{}^3P_2-1\,{}^3P_1'''$
·13 (2)	18249·35	$2\,{}^3P_1-1\,{}^3P_2'''$
·62 (3)	18301·16	$2\,{}^3P_1-1\,{}^3P_1'''$
·26 (2)	18329·21	$2\,{}^3P_1-1\,{}^3P_0'''$
·12 (2)	18336·41	$2\,{}^3P_0-1\,{}^3P_1'''$
·65 (00)	18473·5	
·82 (0)	18569·0	$1\,{}^3S_1'-1\,{}^3D_2$ [18569·34]
·35 (00)	18608·7	
·21 (3)	18682·18	
·15 (1)	18720·87	
8·77 (2)	18725·71	
·75 (4)	18789·13	
·17 (0)	18812·4	
3·47 (1)	18814·87	
8·74 (0)	18867·2	
1·45 (0)	18928·9	
2·49 (00)	18961·1	
0·60 (0)	19004·0	
8·14 (0)	19122·0	
6·63 (0)	19200·95	
9·53 (00)	19227·17	$a\,{}^3D_3'-a\,{}^3F_2'$
0·42 (2)	19260·91	$a\,{}^3D_3'-a\,{}^3F_3'$
4·97 (2)	19281·16	$a\,{}^3D_2'-a\,{}^3F_2'$
3·21 (2)	19287·71	
9·50 (5)	19301·52	$a\,{}^3D_3'-a\,{}^3F_4'$
5·89 (3)	19314·98	$a\,{}^3D_2'-a\,{}^3F_3'$
4·46 (1)	19320·32	
3·37 (2)	19324·39	$a\,{}^3D_1'-a\,{}^3F_2'$
2·32 (1)	19328·32	
71·46 (1)	19331·53	
70·08 (1)	19336·61	
68·24 (1)	19343·57	
94·45 (2)	19585·30	$2\,{}^1S_0'-2\,{}^1P_1'$
76·50 (0)	19693·14	
73·60 (3)	19704·39	$1\,{}^1P_1'-1\,{}^3S_1'$
45·098 (8)	19815·71	$1\,{}^3P_2'-1\,{}^3S_1'$
40·76 (0)	19832·76	$1\,{}^3D_3'-1\,{}^3F_2'$
25·665 (6)	19892·33	$1\,{}^3D_3'-1\,{}^3F_3'$
23·11 (2)	19902·45	
λ, Intensity.	**ν.**	**Classification.**
5016·387 (5)	19929·12	$1\,{}^3D_2'-1\,{}^3F_2'$
5012·026 (2)	19946·46	
5010·620 (6)	19952·06	$1\,{}^3P_1'-1\,{}^3S_1'$
5007·316 (7)	19965·22	$1\,{}^3S_1'-1\,{}^3P_2'''$
5005·140 (10)	19973·90	$1\,{}^3D_3'-1\,{}^3F_4'$
5002·692 (2)	19983·68	$1\,{}^3P_0'-1\,{}^3S_1'$
5001·469 (8)	19988·57	$1\,{}^3D_2'-1\,{}^3F_3'$
5001·128 (7)	19989·92	$1\,{}^3D_1'-1\,{}^3F_2'$
4997·23 (0)	20005·52	
4994·358 (6)	20017·02	$1\,{}^3S_1'-1\,{}^3P_1'''$
4991·22 (2)	20029·61	
4987·377 (4)	20045·04	$1\,{}^3S_1'-1\,{}^3P_0'''$
4957·94 (0)	20164·1	
4895·20 (4)	20422·49	
4860·35 (2)	20568·92	
4810·286 (2)	20783·00	$1\,{}^3D_3'-1\,{}^3D_2$
4806·00 (0)	20801·53	
4803·272 (6)	20813·34	$1\,{}^3D_3'-1\,{}^3D_3$
4793·656 (2)	20855·09	$1\,{}^3D_2'-1\,{}^3D_1$
4788·126 (5)	20879·18	$1\,{}^3D_2'-1\,{}^3D_2$
4781·168 (2)	20909·56	$1\,{}^3D_2'-1\,{}^3D_3$
4779·710 (4)	20915·94	$1\,{}^3D_1'-1\,{}^3D_1$
4774·222 (2)	20939·98	$1\,{}^3D_1'-1\,{}^3D_2$
4765·0 (00)	20980	
4755·5 (00)	21022	
4751·5 (00)	21040	
4735·8 (0)	21110	
4726·9 (00)	21150	
4721·59 (0)	21173·40	
4718·43 (2)	21187·58	
4712·13 (0)	21215·91	
4709·45 (1)	21227·98	$1\,{}^3S_1'-1\,{}^1P_1'''$
4706·41 (0)	21241·70	
4704·33 (0)	21251·09	
4702·57 (0)	21259·04	
4700·12 (0)	21270·12	
4695·91 (1)	21289·19	
4694·55 (3*n*)	21295·36	
4677·93 (3*n*)	21371·01	
4674·98 (2)	21384·50	$1\,{}^1P_1'-2\,{}^3P_0$
4670·0 (0)	21407	
4667·28 (2)	21419·78	$1\,{}^1P_1'-2\,{}^3P_1$
4654·57 (2)	21478·27	$1\,{}^1P_1'-2\,{}^3P_2$
4651·84 (00)	21490·8	
4643·106 (8)	21531·30	$1\,{}^3P_2'-2\,{}^3P_1$
4630·551 (10)	21589·67	$1\,{}^3P_2'-2\,{}^3P_2$
4621·405 (7)	21632·41	$1\,{}^3P_1'-2\,{}^3P_0$
4613·884 (6)	21667·66	$1\,{}^3P_1'-2\,{}^3P_1$
4609·60 (0)	21687·8	
4607·167 (7)	21699·26	$1\,{}^3P_0'-2\,{}^3P_1$
4601·490 (8)	21726·03	$1\,{}^3P_1'-2\,{}^3P_2$
4564·78 (1)	21900·74	$2\,{}^1D_2'-1\,{}^3F_2'$
4552·50 (4)	21959·82	$2\,{}^1D_2'-1\,{}^3F_3'$
4530·37 (5)	22067·08	$2\,{}^1D_2'-1\,{}^1F_3'$?

Table I—(continued).

λ, Intensity.	ν.	Classification.
4507·58 (3)	22178·65	$1\,^3\mathrm{D}_3'-1\,^3\mathrm{P}_2'''$
4488·15 (0)	22274·69	$1\,^3\mathrm{D}_2'-1\,^3\mathrm{P}_2'''$
4477·74 (2)	22326·46	$\mathrm{I}\,^3\mathrm{D}_2'-1\,^3\mathrm{P}_1'''$
[4476·0]	[22335·5]	$1\,^3\mathrm{D}_1'-1\,^3\mathrm{P}_2'''$
4465·54 (0)	22387·44	$1\,^3\mathrm{D}_1'-1\,^3\mathrm{P}_1'''$
4459·96 (1)	22415·44	$1\,^3\mathrm{D}_1'-1\,^3\mathrm{P}_0'''$
4447·035 (10)	22480·60	$2\,^1\mathrm{D}_2'-1\,^1\mathrm{D}_2$?
4441·99 (3*n*)	22506·13	
4433·48 (2*n*)	22549·33	
4432·71 (6*n*)	22553·25	
4431·82 (0)	22557·78	
4427·97 (2)	22577·39	
4427·21 (2)	22581·27	
4426·05 (0)	22587·19	
4402·5 (0*n*)	22708	Very diffuse
4375·00 (0)	22850·74	$2\,^1\mathrm{D}_2'-1\,^3\mathrm{D}_2$
4241·80 (8*n*)	23568·28	
4236·98 (6*n*)	23595·09	
4227·83 (3*n*)	23646·16	$1\,^1\mathrm{P}_1-2\,^1\mathrm{P}_1'$
4215·72 (0)	23714·1	N III ?
4208·12 (00*n*)	23756·9	
4207·51 (1*n*)	23760·4	
4206·57 (0*n*)	23765·7	
4206·35 (00*n*)	23766·9	
4181·17 (0*n*)	23910·0	
4180·89 (0)	23911·6	
4179·68 (1*n*)	23918·6	
4176·17 (3*n*)	23938·7	
4173·75 (0*n*)	23952·6	
4173·51 (0*n*)	23953·9	
4172·04 (00)	23962·4	
4171·63 (2*n*)	23964·7	
4167·50 (0)	23988·5	
4160·8 (0*nn*)	24027	
4156·8 (0*nn*)	24050	
4155·0 (00*n*)	24061	
4145·759 (3)	24114·26	$a\,^3\mathrm{P}_2'-a\,^3\mathrm{S}_1'$
4133·654 (2)	24184·87	$a\,^3\mathrm{P}_1'-a\,^3\mathrm{S}_1'$
4124·10 (1)	24240·90	$a\,^3\mathrm{P}_0'-a\,^3\mathrm{S}_1'$
4110·00 (0*n*)	24324·0	
4092·65 (0*n*)	24427·2	
4087·35 (0*n*)	24458·8	
4082·85 (00)	24485·8	
4082·28 (2*n*)	24489·2	
4076·83 (0*n*)	24522·0	
4073·04 (2*n*)	24544·8	B*
4057·00 (1)	24641·8	
4044·75 (1)	24716·45	
4043·54 (3*n*)	24723·85	B
4041·325 (5*n*)	24737·39	B
4035·090 (4*n*)	24775·62	B
4026·087 (3*n*)	24831·02	B
3994·995 (10)	25024·27	$1\,^1\mathrm{P}_1'-1\,^1\mathrm{P}_1$
3955·851 (6)	25271·88	$1\,^3\mathrm{P}_1'-1\,^1\mathrm{P}_1$
3919·003 (6)	25509·50	$2\,^1\mathrm{D}_2'-1$
3856·07 (3)	25925·81	$2\,^3\mathrm{P}_2-2\,^3\mathrm{P}_1'$
3855·08 (2)	25932·48	$2\,^3\mathrm{P}_1-2\,^3\mathrm{P}_0'$
3847·38 (3)	25984·37	$2\,^3\mathrm{P}_1-2\,^3\mathrm{P}_1'$
3842·20 (3)	26019·40	$2\,^3\mathrm{P}_0-2\,^3\mathrm{P}_1'$
3838·39 (5)	26045·23	$2\,^3\mathrm{P}_2-2\,^3\mathrm{P}_2'$
3829·80 (3)	26103·65	$2\,^3\mathrm{P}_1-2\,^3\mathrm{P}_2'$
3615·88 (1)	27647·94	$1\,^3\mathrm{S}_1'-2\,^3\mathrm{P}_0'$
3609·09 (2)	27699·93	$1\,^3\mathrm{S}_1'-2\,^3\mathrm{P}_1'$
3593·60 (3)	27819·34	$1\,^3\mathrm{S}_1'-2\,^3\mathrm{P}_2'$
3437·162 (6)	29085·46	$1\,^1\mathrm{P}_1'-2\,^1\mathrm{S}_0'$
3408·136 (3)	29333·17	$1\,^3\mathrm{P}_1'-2\,^1\mathrm{S}_0'$
3331·32 (3)	30009·52	$1\,^3\mathrm{D}_2'-2\,^3\mathrm{P}_1'$
3330·30 (2)	30018·70	$1\,^3\mathrm{D}_1'-2\,^3\mathrm{P}_0'$
3328·79 (4)	30032·34	$1\,^3\mathrm{D}_3'-2\,^3\mathrm{P}_2'$
3324·58 (2)	30070·37	$1\,^3\mathrm{D}_1'-2\,^3\mathrm{P}_1'$
3318·14 (2)	30128·72	$1\,^3\mathrm{D}_2'-2\,^3\mathrm{P}_2'$
[3311·5]	[30189·4]	$1\,^3\mathrm{D}_1'-2\,^3\mathrm{P}_2'$
3023·80 (2)	33061·34	
3006·86 (7)	33247·67	$2\,^1\mathrm{D}_2'-2\,^1\mathrm{P}_1'$
2992·81 (0)	33403·71	
2897·49 (3*n*)	34502·5	A*
2892·86 (4*n*)	34557·8	A
2891·05 (1*n*)	34579·4	
2885·25 (6*n*)	34648·9	A
2884·25 (2*n*)	34660·9	A
2879·73 (4*n*)	34715·3	A
2877·66 (2*n*)	34740·3	A
2830·5 (0*nn*)	35319	Very di
2823·67 (4)	35404·51	
2799·20 (4)	35713·99	
2735·0 (1*n*)	36552·3	
2709·82 (6)	36891·9	$2\,^1\mathrm{S}_0-3\,^1\mathrm{P}_1$
2590·91 (4)	38584·9	
2526·93 (0)	39561·8	
[2526·2]	[39572·7]	$2\,^3\mathrm{P}_2-2\,^3\mathrm{D}_1$
2524·55 (1)	39599·1	$2\,^3\mathrm{P}_2-2\,^3\mathrm{D}_2$
2522·51 (1)	39631·1	$2\,^3\mathrm{P}_1-2\,^3\mathrm{D}_1$
2522·27 (4)	39634·9	$2\,^3\mathrm{P}_2-2\,^3\mathrm{D}_3$
2520·85 (3)	39657·8	$2\,^3\mathrm{P}_1-2\,^3\mathrm{D}_2$
2520·27 (2)	39666·4	$2\,^3\mathrm{P}_0-2\,^3\mathrm{D}_1$
2496·88 (4)	40038·0	$2\,^3\mathrm{P}_2-2\,^3\mathrm{P}_2'''$
2494·02 (1)	40083·8	$2\,^3\mathrm{P}_2-2\,^3\mathrm{P}_1'''$
2493·22 (0)	40096·7	$2\,^3\mathrm{P}_1-2\,^3\mathrm{P}_2'''$
2490·37 (2)	40142·6	$2\,^3\mathrm{P}_1-2\,^3\mathrm{P}_1'''$
2488·82 (1)	40167·6	$2\,^3\mathrm{P}_1-2\,^3\mathrm{P}_0'''$
2488·21 (0)	40177·4	$2\,^3\mathrm{P}_0-2\,^3\mathrm{P}_1'''$

* See Table V.

Table I—(continued).

Intensity.	ν.	Classification.
1·30 (3)	40616·6	$1\,{}^1P_1-3\,{}^1P_1'$
4·00 (0)	41241·6	
8·87 (0*n*)	41329·0	
15·79 (0)	41381·7	
11·13 (0)	41461·7	
2·45 (0)	41611·5	
0·13 (0)	41651·7	
8·75 (0)	41675·7	
7·10 (0)	41704·4	
5·67 (00)	41729·3	
4·99 (0)	41741·1	
0·90 (2)	41812·5	$1\,{}^3S_1'-2\,{}^3P_2'''$
8·24 (1)	41859·0	$1\,{}^3S_1'-2\,{}^3P_1'''$
6·80 (0)	41884·8	$1\,{}^3S_1'-2\,{}^3P_0'''$
7·01 (3)	43145·9	
·66 (1)	43152·4	
6·46 (2)	43156·1	
·54 (1*n*)	43191·8	
1·60 (1)	43246·8	
0·61 (1)	43265·3	
8·90 (5)	43297·3	
8·55 (5)	43303·9	
0·69 (0)	43451·9	
·97 (0)	43484·3	
3·40 (2)	43589·9	$\left\{ 2\,{}^3P_2-3\,{}^3P_1' ; \quad 1\,{}^3D_3'-2\,{}^3D_2 \right.$
2·72 (1)	43602·8	$2\,{}^3P_1-3\,{}^3P_0'$
1·67 (2)	43622·8	$1\,{}^3D_3'-2\,{}^3D_3$
0·31 (1)	43648·7	$2\,{}^3P_1-3\,{}^3P_1'$
9·9]	[43656·5]	$1\,{}^3D_2'-2\,{}^3D_1$
8·47 (3)	43683·8	$\left\{ 2\,{}^3P_0-3\,{}^3P_1' ; \quad 1\,{}^3D_2'-2\,{}^3D_2 \right.$
6·73 (4)	43717·0	$\left\{ 2\,{}^3P_2-3\,{}^3P_2' ; \quad 1\,{}^3D_1'-2\,{}^3D_1 ; \quad 1\,{}^3D_2'-2\,{}^3D_3 \right.$
5·3]	[43743·8]	$1\,{}^3D_1'-2\,{}^3D_2$
3·70 (2)	43775·0	$2\,{}^3P_1-3\,{}^3P_2'$
8·91 (2)	44650·8	
7·21 (0*n*)	44684·8	
6·78 (0*n*)	44693·3	
5·18 (1)	44725·3	
1·65 (0)	44796·0	
19·58 (0)	45039·6	
06·10 (3)	45314·7	$1\,{}^3S_1'-3\,{}^3P_0'$ (in part)
03·72 (1)	45363·6	$1\,{}^3S_1'-3\,{}^3P_1'$
97·58 (2)	45489·9	$1\,{}^3S_1'-3\,{}^3P_2'$

λ, Intensity.	ν.	Classification.
*2096·79 (3)	47676·7	$1\,{}^3D_2'-3\,{}^3P_1'$
2096·16 (2)	47691·0	$1\,{}^3D_1'-3\,{}^3P_0'$
2095·47 (6)	47706·8	$1\,{}^3D_3'-3\,{}^3P_2'$
2094·12 (2)	47737·4	$1\,{}^3D_1'-3\,{}^3P_1'$
2091·20 (3)	47804·2	$1\,{}^3D_2'-3\,{}^3P_2'$
[2088·5]	[47864·4]	$1\,{}^3D_1'-3\,{}^3P_2'$
1886·82 (4)	52981·5	
1877·97 (2)	53231·1	
1868·50 (1)	53500·8	
1867·58 (0)	53527·2	
[1863·7]	[53637·6]	$1\,{}^3P_2'-2\,{}^3D_1'$
1861·94 (2)	53689·2	$1\,{}^3P_2'-2\,{}^3D_2'$
[1859·0]	[53774·0]	$1\,{}^3P_1'-2\,{}^3D_1'$
1858·59 (5)	53786·0	$1\,{}^3P_2'-2\,{}^3D_3'$
1857·84 (2)	53807·7	$1\,{}^3P_0'-2\,{}^3D_1'$
1857·14 (3)	53826·3	$1\,{}^3P_1'-2\,{}^3D_2'$
λ, Vac.		
1836·36 (1)	54455·5	$1\,{}^3P_2'-2\,{}^3S_1'$
1831·78 (0)	54591·7	$1\,{}^3P_1'-2\,{}^3S_1'$
1830·71 (00)	54623·6	$1\,{}^3P_0'-2\,{}^3S_1'$
1766·08 (1)	56622·6	
1765·13 (1)	56653·0	
1763·63 (2)	56701·2	
†1751·75 (10)	57085·7	? N I
‡1747·855 (7)	57213·0	$1\,{}^1S_0'-1\,{}^3P_1'$
1743·22 (2)	57365·1	$\beta\,{}^3P'_{12}-1\,{}^3D_2'$
‡1740·315 (5)	57460·9	$1\,{}^1S_0'-1\,{}^1P_1'$
1675·83 (5)	59671·9	$\beta\,{}^3P'_{012}-1\,{}^3S_1'$
1629·86 (0)	61355·0	$\beta\,{}^3P_{12}'-2\,{}^3P_0$
1629·02 (1)	61386·6	$\beta\,{}^3P_{012}'-2\,{}^3P_1$
1627·42 (1)	61447·0	$\beta\,{}^3P_{12}'-2\,{}^3P_2$
1616·06 (1*n*)	61878·9	
1590·25 (2*n*)	62883·2	
1574·28 (1*n*)	63521·1	
1573·21 (1*n*)	63564·3	
1411·99 (4)	70822·0	
1346·41 (0)	74271·6	$\beta\,{}^3D_{12}-1\,{}^3D_1'$
1345·29 (1)	74332·9	$\beta\,{}^3D_{12}-1\,{}^3D_2'$
1343·37 (2)	74439·7	$\beta\,{}^3D_3-1\,{}^3D_3'$
1330·80 (00)	75142·8	
1329·43 (0)	75220·2	
1328·01 (1)	75300·6	
1326·67 (2)	75376·7	
1319·85 (5)	75766·2	? N I
1319·10 (2)	75809·3	
1310·89 (5*n*)	76282·9	

The following lines in this group have been omitted as probably being due to N III: 2099·87 (47606·8), 7·74 (47655·2), 2097·25 (47667·3), 2091·95 (47787·0).

There is a carbon line at λ 1751·33.

λλ by Bowen and Ingram. Assigned to N II by authors from experimental behaviour.

Table I—(continued).

λ, Vac.	ν.	Classification.
		Bowen.
*1276·74 (1)	78324·5	$\beta\,{}^3D_1-2\,{}^3P_0$; $b\,D_{12}-3mP_0$
*1276·18 (2)	78358·9	$\beta\,{}^3D_2-2\,{}^3P_1$; $b\,D_{12}-3mP_1$
*1275·06 (3)	78427·7	$\beta\,{}^3D_3-2\,{}^3P_2$; $b\,D_3\ -3mP_2$
1258·75 (3)	79444	
1243·14 (7)	80442	? N I
1242·67 (4)	80472	
1229·7 (4*n*)	81321	Nebulous group, probably more complex. N II ?
1226·4 (4*n*)	81539	
1224·2 (3)	81686	
†1200·681 (1)	83286·1	
†1200·200 (2)	83319·4	
†1199·533 (3)	83365·8	
†1134·987 (3)	88106·7	
†1134·420 (3)	88150·8	
†1134·180 (2)	88169·4	
		Bowen.
*1085·701 (8)	92106·4	$1\,{}^3P_2-\beta\,{}^3D_3$; $a\,P_2-b\,D_3$
*1085·540 (3)	92120·1	$1\,{}^3P_2-\beta\,{}^3D_{12}$; $a\,P_2-b\,D_{12}$
*1084·566 (7)	92202·8	$1\,{}^3P_1-\beta\,{}^3D_{12}$; $a\,P_1-b\,D_{12}$
*1083·983 (6)	92252·4	$1\,{}^3P_0-\beta\,{}^3D_1$; $a\,P_0-b\,D_1$

λ, Vac.	ν.	Classification.
*916·698 (8)	109087·2	$a\,P_2-b\,P_2$
*916·018 (6)	109168·2	$a\,P_1-b\,P_2$
*915·963 (6)	109174·7	$a\,P_1-b\,P_1$
*915·603 (6)	109217·6	$a\,P_0-b\,P_1$
*672·026 (2)	148803·8	$1\,{}^3P_2-1\,{}^3P_1'$; $a\,P_2-3$
*671·780 (2)	148858·3	$1\,{}^3P_1-1\,{}^3P_0'$; $a\,P_1-3$
*671·650 (1)	148887·1	$1\,{}^3P_1-1\,{}^3P_1'$; $a\,P_1-3$
*671·397 (3)	148943·2	$1\,{}^3P_{02}-1\,{}^3P_{12}'$; $a\,P_{02}-3$
*671·027 (2)	149025·3	$1\,{}^3P_1-1\,{}^3P_2'$; $a\,P_1-3$
*645·180 (5)	154995·5	$1\,{}^3P_2-\beta\,{}^3S_1$; $a\,P_2-b\,S$
*644·836 (5)	155078·2	$1\,{}^3P_1-\beta\,{}^3S_1$; $a\,P_1-b\,S$
*644·633 (4)	155127·0	$1\,{}^3P_0-\beta\,{}^3S_1$; $a\,P_0-b\,S$
*533·71 (3)	187368	$1\,{}^3P_2-1\,{}^3D_3$; $a\,P_2-3$
*533·53 (3)	187431	$1\,{}^3P_{01}-1\,{}^3D_{12}$; $a\,P_{01}-3$

* λλ and classification by Bowen (' Phys. Rev.,' vol. 29, p. 231, Feb., 1927).
† λλ by Bowen and Ingram. Assigned to N II by authors from experimental behaviour.

Term Notation.

Pending a more general agreement as to the notation and numeration of spectroscopic terms, it is necessary to explain the procedure which is followed in the present communication. A spectrum like that of N II, which is derived from singlet and triplet terms, could be effectively described by the use of the earlier notation, in which capital letters (S, P, D, etc.) were used for singlet, and small letters (*s*, *p*, *d*, etc.) for triplet terms. There is, however, a strong tendency towards the description of all spectra by the same generalised notation, and to use capital letters exclusively for the representation of term types.[*]

In this notation, which is adopted in the present paper, the multiplicity of the system to which a term belongs is indicated by an index number on the upper left of the term symbol, and the inner quantum number by a suffix on

[*] This is the more necessary now as small letters, *s*, *p*, *d*, etc., are used by some authors to indicate the *k* values of electron orbits.

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the lower right. Thus, the P terms of a triplet system are represented by $^3P_2$, $^3P_1$, $^3P_0$. So far, there will probably be general agreement, but the designation of individual terms or groups of terms is more debatable. In the spectra of atoms having more than a single valence electron, the occurrence of two or more sets of terms of the same type, which was revealed especially by the work of Russell and Saunders on the alkaline earths,* is emphasised by the recent theoretical developments. Thus, as is now well known, we may find numerous terms of each of the types S, P, D ... , which may be recognised as such by their respective contributions to Zeeman patterns, but not all of which have the same combining properties. Each class of terms is divisible into two groups, distinguished by the use of dashes, as S, S′; P, P′; D, D′, and so on; the S, P, D... terms combine among themselves in accordance with the older selection rules, as do also the S′, P′, D′ terms. The two classes of terms, however, intercombine in accordance with the modified selection rule $\Delta l = 0$,† as for example P P′, D D′; other previously unexpected combinations, such as P F″, are also possible. Each group of terms may sometimes be further subdivided so as to indicate Rydberg sequences; thus, one set of P terms constitutes the P sequence and another the P″ sequence, while the P′ terms may similarly be divided into P′ and P‴ sequences. According to the new theory, there is no difference at all between such P, P″, P′ or P‴ terms, and the notation merely expresses properties which are more fundamentally indicated by electron configurations.

The new theory indicates that in general the structure of the spectrum of an element does not depend solely upon a single electron, as in the earlier theory applicable to the alkali metals, but represents the resultant effect of *all* the electrons; or, since the resultant of the underlying electrons which belong to completed n_k groups or "shells" is zero, the terms, or energy levels, are determined by all the electrons which form parts of uncompleted shells. In the general case, a given configuration of electrons gives rise to a group of terms, differing in energy value among themselves (but not greatly), these differences being accounted for by the different orientations of the corresponding orbits. In the case of N II, the two electrons which are concerned in the production of at least the greater part of the spectrum are normally in 2_2 orbits, and the corresponding theoretical terms are $^3P_{012}$, $^1D_2$, $^1S_0$, which are completely specified by writing $(2_2\,2_2)\,^3P_{012}$, $(2_2\,2_2)\,^1D_2$, $(2_2\,2_2)\,^1S_0$. The next set of terms, $^3P_{012}$, $^1P_1$, arise when one of the electrons occupies a 3_1 orbit while the other remains in 2_2, and these may be similarly represented by $(2_2\,3_1)\,{}^3P_{012}$, $(2_2\,3_1)\,{}^1P_1$. Transitions between the two sets of levels give rise to spectrum lines which may be represented by writing, for example, $(2_2\,2_2)\,{}^3P_2-(2_2\,3_1)\,{}^1P_1$. In this notation there is no necessity to "dash" any of the terms, as the possibility of combinations is already indicated by selection rules applicable to the electron transitions. These rules are as follows :—

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* 'Astrophys. J.,' vol. 61, p. 38 (1925).

† l indicates the term type, being 1 for S, 2 for P, 3 for D, and so on. It is related to the vector sum of the k values of all the electrons which contribute to the spectrum.

(1) Not more than two electrons make simultaneous transitions from one n_k orbit to another.

(2) The transitions are restricted to those for which $\Delta k = \pm 1$ for one of the electrons and $\Delta k = 0$, or ± 2 for the other.

(3) All combinations are further subject to the inner quantum selection rule, $\Delta j = 0, \pm 1$, with $j = 0 \rightarrow j = 0$ forbidden.

Rydberg sequences would be formed from successive terms such as $(2_2\,2_2)$, $(2_2\,3_2)$, $(2_2\,4_2)$, and so on.

While this notation undoubtedly conveys all necessary information with regard to the electron configurations, term types, possible Rydberg sequences and combination possibilities, it is very doubtful whether it is the most convenient for general descriptive purposes. It seems to the writers to be unnecessarily cumbersome for writing and printing,* and to be less convenient for use in the actual analysis of a spectrum than the system mentioned above, in which the combination properties of the various terms are more readily perceived. In the present paper, the older notation has accordingly been adopted, but it will be a simple matter to convert this to the electronic designations, if desired.

As regards the numeration of terms, the deepest term of each class has been numbered 1, the next deepest 2, and so on, in the case of terms which arise when only one electron is displaced from its normal orbit ; terms which originate in the simultaneous displacement of both of the 2_2 electrons are distinguished by the similar use of *a*, *b*, *c* for a sequence of terms of the same class, *a* being the deepest.

The selection rules applicable to the adopted system of notation, as deduced from those which serve for the electron transitions, are as follows :—

(1) Within one class of terms (*i.e.*, "dashed" or "undashed") $\Delta l = \pm 1$ or ± 3, the latter usually yielding only faint lines.

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* The existence of quintet terms, as discovered in the analogous spectrum of O III by Mihul ('Comptes Rendus,' vol. 184, p. 89 (1927)), would still further complicate the electronic notation.

(2) Between the two classes $\Delta l = 0$, or ± 2, lines due to the latter transitions usually being faint.

(3) $\Delta j = 0, \pm 1$, with $j = 0 \rightarrow j = 0$ forbidden.

Predicted Terms of N II.

For transitions of a single electron the terms predicted by theory are indicated in Table II. They have been deduced by the application of Hund's rules, supplemented by data given by Laporte.* The unexcited atom of singly-ionised nitrogen has a structure similar to that of neutral carbon (atomic number $= 6$), and as shown in Table II, two electrons are in the K, or 1_1 group and four in the L group; two of the latter are in 2_1 orbits, and two in 2_2 orbits. The first four thus occur in completed groups [the number required to complete a group being $2(2k - 1)$] and only the electrons in 2_2 orbits need at present be considered.

In the first instance (Table II), one of the two outer electrons is supposed to remain in its 2_2 orbit (*i.e.*, $\Delta k = 0$ for this electron), and the table shows the different groups of terms which arise as the other electron occupies successively larger orbits. Usually, the deepest term of the group arising from a given configuration is that having the largest multiplicity and the largest l value, but this rule is not always followed in the case of N II, and other exceptions have been recorded.

The predicted terms are named so as to indicate the combining properties in accordance with the notation already described, and are also arranged to show the various Rydberg sequences. Terms which have actually been identified are printed in heavy type.

The predictions have aided in the analysis of the spectrum beyond that noted in the previous paper by indicating in the first instance the character of the deepest terms, and next by giving approximate values of unidentified terms and thence some idea of the location of multiplets arising from their combinations with terms already known. It will be observed that there is excellent agreement between observation and theory, so far as the comparison can at present be made.

The "core" of the atom of N II is the normal state of the atom of N III and is similar in structure to the neutral atom of boron, having two 1_1, two 2_1, and one 2_2 electrons. The terms corresponding to this configuration are $^2P_1$ and $^2P_2$, of which the former is the deeper. All the terms given in Table II are based upon these two states of the core, and from Hund's rules it may be determined which of the various sequences are based upon $^2P_1$ and which upon $^2P_2$. Thus :—

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* *Loc. cit.*

Based upon $^2P_2$ state of core :

$^3S_1'$ $^3P_2$ $^3P_2'$ $^3P'''_{012}$ $^3D_3$ $^3D_3'$ $^3D'''_{123}$ $^3F_4$ $^3F_4'$ $^3G_5'$

Based upon $^2P_1$ state of core :

$^3P_{01}$ $^3P'_{01}$ $^3D_{12}$ $^3D'_{12}$ $^3F_{23}$ $^3F'_{23}$ $^3G'_{34}$.

All singlets are based upon the $^2P_2$ state of the core.

It should be noted that the dashed and undashed terms of the previous paper have been interchanged, in order to make the probable deepest term of the

Table II.—Predicted and

K	L		M			N				O		Triplet Terms.									
1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1											
2	2	2									2_2 2_2							**1 ^{3}P**			
2	2	1	1								2_2 3_1										**1 ^{3}P′**
2	2	1		1							2_2 3_2				**1 ^{3}D′**			**2 ^{3}P**		**1 ^{3}S$_1$′**	
2	2	1			1						2_2 3_3		**1 ^{3}F′**				**1 ^{3}D**		**1 ^{3}P‴**		
2	2	1				1					2_2 4_1										**2 ^{3}P′**
2	2	1					1				2_2 4_2				**2 ^{3}D′**			**3 ^{3}P**		**2 ^{3}S$_1$′**	
2	2	1						1			2_2 4_3		2 ^{3}F′				**2 ^{3}D**		**2 ^{3}P‴**		
2	2	1							1		2_2 4_4	1 ^{3}G′		1 ^{3}F		1 ^{3}D‴					
2	2	1								1	2_2 5_1										**3 ^{3}P′**

*$1\,^3P_0 = 238849$		$1\,^3P_0' = 89937{\cdot}33$		$1\,^3P_0''' = 49908{\cdot}75$		$1\,^3D_1' = 72324{\cdot}22$	
	50		*31·60*		*−28·06*		*60·7*
$1\,^3P_1 = 238799$		$1\,^3P_1' = 89905{\cdot}73$		$1\,^3P_1''' = 49936{\cdot}81$		$1\,^3D_2' = 72263{\cdot}44$	
	84		*136·36*		*−51·80*		*96·1*
$1\,^3P_2 = 238715$		$1\,^3P_2' = 89769{\cdot}37$		$1\,^3P_2''' = 49988{\cdot}61$		$1\,^3D_3' = 72167{\cdot}25$	
$2\,^3P_0 = 68273{\cdot}32$		$2\,^3P_0' = 42305{\cdot}61$		$2\,^3P_0''' = 28079{\cdot}7$		$2\,^3D_1' = 36131{\cdot}76$	
	35·25		*51·79*		*−25·5*		*50·9*
$2\,^3P_1 = 68238{\cdot}07$		$2\,^3P_1' = 42253{\cdot}82$		$2\,^3P_1''' = 28095{\cdot}2$		$2\,^3D_2' = 36080{\cdot}84$	
	58·37		*119·29*		*−46·1*		*96·2*
$2\,^3P_2 = 68179{\cdot}70$		$2\,^3P_2' = 42134{\cdot}53$		$2\,^3P_2''' = 28141{\cdot}3$		$2\,^3D_3' = 35984{\cdot}64$	
$3\,^3P_2 = [35075]$		$3\,^3P_0' = 24634{\cdot}3$		$3\,^3P_2''' = [17968]$		$3\,^3D_3' = [21620]$	
			45·8				
		$3\,^3P_1' = 24588{\cdot}5$					
			127·1				
		$3\,^3P_2' = 24461{\cdot}4$					
		$4\,^3P_2' = [15980]$					

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* Identified by Bowen (see Addendum).

undashed type, in accordance with the conventional procedure. The older suffixes have also been replaced by inner quantum numbers, so that, including singlet terms, the relation of the earlier to the present notation is as follows :—

$p_3 = 1\,{}^3\mathrm{P}_0'$ $p_3' = 2\,{}^3\mathrm{P}_0$ $d_3' = 1\,{}^3\mathrm{D}_1$
$p_2 = 1\,{}^3\mathrm{P}_1'$ $p_2' = 2\,{}^3\mathrm{P}_1$ $d_2' = 1\,{}^3\mathrm{D}_2$
$p_1 = 1\,{}^3\mathrm{P}_2'$ $p_1' = 2\,{}^3\mathrm{P}_2$ $d_1' = 1\,{}^3\mathrm{D}_3$

$p_3^2 = 2\,{}^3\mathrm{P}_0'$ $d_3 = 1\,{}^3\mathrm{D}_1'$ $s = 1\,{}^3\mathrm{S}_1'$
$p_2^2 = 2\,{}^3\mathrm{P}_1'$ $d_2 = 1\,{}^3\mathrm{D}_2'$ $\mathrm{P} = 1\,{}^1\mathrm{P}_1'$
$p_1^2 = 2\,{}^3\mathrm{P}_2'$ $d_1 = 1\,{}^3\mathrm{D}_3'$ $\mathrm{S} = 1\,{}^1\mathrm{P}_1$
$\mathrm{S}^2 = 2\,{}^1\mathrm{S}_0'$

Observed Terms of N II.

Singlet Terms.											Term Values.
		$1\,{}^1\mathrm{D}_2'$							$1\,{}^1\mathrm{S}_0'$		238849—147119
										$1\,{}^1\mathrm{P}_1'$	89937— 89658
		$2\,{}^1\mathrm{D}_2'$					$1\,{}^1\mathrm{P}_1$		$2\,{}^1\mathrm{S}_0'$		74235— 60572
	$1\,{}^1\mathrm{F}'_3$				$1\,{}^1\mathrm{D}_2$			$1\,{}^1\mathrm{P}_1'''$			52334— 48725
										$2\,{}^1\mathrm{P}'_1$	42305— 40987
		$3\,{}^1\mathrm{D}_2$					$2\,{}^1\mathrm{P}_1$		$3\,{}^1\mathrm{S}_0'$		36132
	$2\,{}^1\mathrm{F}_3'$				$2\,{}^1\mathrm{D}_2$			$2\,{}^1\mathrm{P}_1'''$			28607
$1\,{}^1\mathrm{G}_4'$			$1\,{}^1\mathrm{F}_3$	$1\,{}^1\mathrm{D}_2'''$							
										$3\,{}^1\mathrm{P}_1'$	24634

${}^3\mathrm{D}_1 = 51408{\cdot}36$
24·04
${}^3\mathrm{D}_2 = 51384{\cdot}32$
30·34
${}^3\mathrm{D}_3 = 51353{\cdot}98$

${}^3\mathrm{D}_1 = 28606{\cdot}9$
26·5
${}^3\mathrm{D}_2 = 28580{\cdot}4$
35·6
$2\,{}^3\mathrm{D}_3 = 28544{\cdot}8$

$3\,{}^3\mathrm{D}_3 = [18130]$

$1\,{}^3\mathrm{F}_2' = 52334{\cdot}32$
59·42
$1\,{}^3\mathrm{F}_3' = 52274{\cdot}90$
81·55
$1\,{}^3\mathrm{F}_4' = 52193{\cdot}35$

$2\,\mathrm{F}_4' = [28855]$

$1\,{}^3\mathrm{S}_1' = 69953{\cdot}66$
$2\,{}^3\mathrm{S}_1' = 35313{\cdot}9$
$3\,{}^3\mathrm{S}_1' = [21570]$

$1\,{}^1\mathrm{P}_1' = 89657{\cdot}96$
$2\,{}^1\mathrm{P}_1' = 40987{\cdot}42$
$3\,{}^1\mathrm{P}_1' = 24018{\cdot}7$

$1\,{}^1\mathrm{P}_1 = 64633{\cdot}77$
$2\,{}^1\mathrm{P}_1 = [33753]$

$1\,{}^1\mathrm{F}_3' = 52168{\cdot}02$?

$1\,{}^1\mathrm{D}_2 = 51754{\cdot}50$?

$1\,{}^1\mathrm{P}_1''' = 48725{\cdot}55$

$1\,{}^1\mathrm{D}_2' = > 210000$
$2\,{}^1\mathrm{D}_2' = 74235{\cdot}10$
$3\,{}^1\mathrm{D}_2' = [37270]$

$1\,{}^1\mathrm{S}_0' = 147118{\cdot}8$
$2\,{}^1\mathrm{S}_0' = 60572{\cdot}53$
$3\,{}^1\mathrm{S}_0' = [32407]$

Triplet Term Values.

Although no long sequences of terms occur in the spectrum of N II, it is possible to determine the absolute values of the terms with considerable accuracy because of the identification of three ${}^3P{}^3P'$ multiplets which form a Rydberg sequence. Thus, we find

$$\begin{aligned} 2\,{}^3P_2 - 1\,{}^3P_2' &= -21589\cdot67 \\ 2\,{}^3P_2 - 2\,{}^3P_2' &= 26045\cdot23 \\ 2\,{}^3P_2 - 3\,{}^3P_2' &= 43717\cdot0 \end{aligned}$$

Taking 109678·3 as the value of the series constant, R, these lines are represented by the formula

$$\nu = 68179\cdot70 - 4R/[m + 0\cdot259020 - 0\cdot096678/m]^2$$

giving

$$1\,{}^3P_2' = 89769\cdot37 \qquad 2\,{}^3P_2 = 68179\cdot70.$$

The remaining term values are then derived in the usual way from the combinations in which they appear, with the results shown in the lower part of Table II.*

It should be noted that two successive Rydberg terms have been identified for ${}^3S_1$, ${}^3P'''$, ${}^3D'$, and ${}^3D$. Formulæ for these terms may accordingly be computed for purposes of extrapolation. Thus, we find

$$\begin{aligned} m\,{}^3S_1' &= 4R/[m + 0\cdot465402 + 0\cdot177780/m]^2 \\ m\,{}^3P_2''' &= 4R/[m + 0\cdot918807 + 0\cdot087336/m]^2 \\ m\,{}^3D_3' &= 4R/[m + 0\cdot543799 - 0\cdot156426/m]^2 \\ m\,{}^3D_3 &= 4R/[m + 0\cdot915447 + 0\cdot014760/m]^2 \end{aligned}$$

The correcting terms in these formulæ are quite small, and if this be also true of the sequences of which only one term has been identified, roughly approximate values of additional terms may be derived by the calculation of simple Rydberg formulæ. Thus

$$\begin{aligned} m\,{}^3P &= 4R/[m + 0\cdot536663]^2 \\ m\,F_4' &= 4R/[m + 0\cdot899230]^2 \end{aligned}$$

Terms which have been calculated from the formulæ are included in Table II, where they are enclosed in square brackets. Combinations involving such computed terms, however, have not been traced, and it is evident that they must either be absent or very faint.

The formula for $m\,{}^3P$ is of particular interest because the deepest of all the terms is expected to be of this type. The formula gives for the first term of this sequence ($m = 1$) the value 185,780, as first pointed out by Laporte. This suggests the occurrence of a multiplet $1\,^3P_{012} - 1\,^3P'_{012}$ in the neighbourhood of ν 96,000 and a triplet $1\,^3P_{012} - 1\,^1P_1'$ in close proximity, since $1\,^1P'$ and $1\,^3P'$ are but slightly different in value (see later). Bowen and Millikan* have already assigned a triplet to N II, on the ground of its separations and position in the spectrum, namely, according to the more recent measures of Bowen and Ingram :—

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* If R_∞ (=109737) be preferred to R_H (= 109678·3) all the term values should be increased by about 4 units.

λ	ν	$\Delta\nu$
916·690 (4)	109088·1	
		83·9
915·986 (4)	109172·0	
		46·6
915·595 (3)	109218·6	

If this be taken as $1\,^3P_{012} - 1\,^1P_1'$, the value of $1\,^3P_0$ would be 198,876, and the corresponding ionisation potential would be 24·5 volts, in close agreement with the 24 volts estimated from stellar spectra.†

There are, however, no indications in the published lists of nitrogen lines in this region, or in our own plates, of such an adjacent multiplet as would be expected. The photographs of this region given by Hopfield and Leifson‡ also give no indications of such a multiplet. The above identification of the $1\,^3P_{012} - 1\,^1P'$ triplet is consequently very doubtful; the multiplet would, indeed, be expected to be more intense than the triplet, as in the case of the multiplet $1\,^3P'_{012} - 2\,^3P_{012}$ and the adjacent triplet $1\,^1P' - 2\,^3P_{012}$ (near λ 4640). It is, in fact, very doubtful whether there is actually a *triplet* of N II in the position given by Millikan and Bowen. Our own plates of vacuum tube spectra, both with strong and weak discharges, show only two lines, apparently agreeing in position with the two more refrangible members of the supposed triplet. Further, Hopfield and Leifson, who also used vacuum tubes, have similarly tabulated only these two lines [$\lambda\lambda$ 916·03 (2), 915·59 (3)]. It may be, therefore, that the λ 916·69 component of the supposed triplet is really a line special to the "hot spark" conditions under which Millikan and Bowen's photographs were taken.

Further investigations of the spectrum in the region beyond λ 830 (ν 120480) thus appear to be necessary before final conclusions can be reached with regard to the deepest terms. From the available evidence, it would seem that the

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* 'Phys. Rev.,' vol. 24, p. 221 (1924).

† R. H. Fowler and E. A. Milne, 'Monthly Notices R.A.S.,' vol. 84, p. 499 (1924).

‡ 'Astrophys. Journ.,' vol. 58, p. 59 (1923).

$1\,^3P - 1\,^1P'$ and $1\,^3P - 1\,^3P'$ lines lie beyond this limit and that the value of $1\,^3P$ is greater than 210420 (=120480 + 89940); that is, the ionisation potential must be greater than 26 volts.*

Triplet Combinations.

The combinations arising from terms of the triplet system due to the changing orbits of a single electron are shown in Table III. The table includes the combinations noted in the previous paper, but some of the wave-lengths have been revised, and repetition is also necessary on account of the amended notation.

The terms are uniformly arranged in increasing order from left to right, and in decreasing order downwards in each group of similar type. Wave-numbers enclosed in brackets are computed values. Inverted terms are indicated by the negative signs of $\Delta\nu$.

On account of experimental difficulties, arising partly from the long exposures required for vacuum tubes with instruments of large dispersion, and partly from the instability of some of the wave-lengths, there are slight differences in the values of the same terms derived from different combinations. The values deduced from the sets of measures judged to be the most trustworthy

Table III.—Triplet Combinations.

Term Values.	$1\,^3P_2'$ 89769·37	*136·36*	$1\,^3P_1'$ 89905·73	*31·60*	$1\,^3P_0'$ 89937·33	Combinations.
$2\,^3P_0$ = 68273·32			21632·41 (7)			
35·25			*35·25*			
$2\,^3P_1$ = 68238·07	21531·30 (8)	*136·36*	21667·66 (6)	*31·60*	21699·26 (7)	$1\,^3P' - 2\,^3P$
58·37	*58·37*		*58·37*			
$2\,^3P_2$ = 68179·70	21589·67 (10)	*136·36*	21726·03 (8)			
$1\,^3D_1'$ = 72324·22	17445·14 (2)	*136·40*	17581·54 (6)	*31·56*	17613·10 (6)	$1\,^3P' - 1\,^3D'$
60·78	*60·82*		*60·72*			
$1\,^3D_2'$ = 72263·44	17505·96 (6)	*136·30*	17642·26 (8)			
96·19	*96·16*					
$1\,^3D_3'$ = 72167·25	17602·12 (10)					
$2\,^3D_1'$* = 36131·76	[53637·6]		[53774·0]		53807·7 (3)	$1\,^3P' - 2\,^3D'$
50·92						
$2\,^3D_2'$ = 36080·84	53689·2 (2)	*137·1*	53826·3 (3)			
96·20	*96·8*					
$2\,^3D_3'$ = 35984·64	53786·0 (5)					
$1\,^3S_1'$ = 69953·66	19815·91 (8)	*136·35*	19952·06 (6)	*31·62*	19983·68 (2)	$1\,^3P' - 1\,^3S'$
$2\,^3S_1'$ = 35313·9	54455·5 (1)	*136·2*	54591·7 (0)	*31·9*	54623·6 (00)	$1\,^3P' - 2\,^3S'$

* Term values adopted from $1\,^3F' - 2\,^3D'$.

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* See Addendum.

Table III—(continued).

Term Values.	$1\,^3D_3'$ 72167·25		$1\,^3D_2'$ 72263·44		$1\,^3D_1'$ 72324·22	Combinations.
$1\,^3D_1$ = 51408·32			20855·09 (2)	*60·85*	20915·94 (4)	
24·07			*24·09*		*24·04*	
$1\,^3D_2$ = 51384·25	20783·00 (2)	*96·18*	20879·18 (5)	*60·80*	20939·98 (2)	$1\,^3D' - 1\,^3D$
30·35	*30·24*		*30·38*			
$1\,^3D_3$ = 51353·90	20813·34 (6)	*96·22*	20909·56 (2)			
$^3D_1$* = 28606·95			[43656·5]		†43717·0 (4)	
26·52						
$2\,^3D_2$ = 28580·43	†43589·9 (2)		†43683·8 (3)		[43743·8]	$1\,^3D' - 2\,^3D$
35·63						
$^3D_3$ = 28544·80	43622·8 (2)		†43717·0 (4)			
$2\,^3P_0'$ = 42305·52					30018·70 (2)	
51·63					*51·67*	
$2\,^3P_1'$ = 42253·89			30009·52 (3)	*60·85*	30070·37 (2)	$1\,^3D' - 2\,^3P'$
119·07			*119·20*			
$^3P_2'$ = 42134·82	30032·34 (4)	*96·38*	30128·72 (2)		[30189·4]	
$^3P_0'$ = 24633·2					47691·0 (2)	
45·9					*46·4*	
$^3P_1'$ = 24587·3			47676·7 (3)	*60·7*	47737·4 (2)	$1\,^3D' - 3\,^3P'$
127·5			*127·5*			
$^3P_2'$ = 24459·8	47706·8 (6)	*97·4*	47804·2 (3)		[47864·4]	
$^3F_2'$ = 52334·32	19832·76 (0)	*96·36*	19929·12 (5)	*60·80*	19989·92 (7)	
59·42	*59·57*		*59·45*			
$1\,^3F_3'$ = 52274·90	19892·33 (6)	*96·24*	19988·57 (8)			$1\,^3D' - 1\,^3F'$
81·55	*81·57*					
$^3F_4'$ = 52193·35	19973·90 (10)					
$1\,^3P_2'''$ = 49988·67	22178·65 (3)	*96·04*	22274·69 (0)		[22335·55]	
−51·79			*51·77*			
$1\,^3P_1'''$ = 49936·88			22326·46 (2)	*60·98*	22387·44 (0)	$1\,^3D' - 1\,^3P'''$
−28·10					*28·00*	
$1\,^3P_0'''$ = 49908·78					22415·44 (1)	

* Term values adopted from $2\,^3P - 2\,^3D$.
† Superposed on lines of $2\,^3P - 3\,^3P'$.

Table III—(continued).

Term Values.	$2\,^3\mathrm{P}_2$ 68179·70	*58·37*	$2\,^3\mathrm{P}_1$ 68238·07	*35·25*	$2\,^3\mathrm{P}_0$ 68273·32	Combinations
$1\,^3\mathrm{D}_1$ = 51408·40	16771·27 (0)	*58·39*	16829·66 (2)	*35·29*	16864·95 (4)	$2\,^3\mathrm{P} - 1\,^3\mathrm{D}$
24·01	*24·06*		*24·00*			
$1\,^3\mathrm{D}_2$ = 51384·39	16795·33 (3)	*58·33*	16853·66 (7)			
30·32	*30·30*					
$1\,^3\mathrm{D}_3$ = 51354·07	16825·63 (8)					
$2\,^3\mathrm{D}_1$ = 28606·9	[39572·7]		39631·1 (1)	*35·3*	39666·4 (2)	$2\,^3\mathrm{P} - 2\,^3\mathrm{D}$
26·5			*26·7*			
$2\,^3\mathrm{D}_2$ = 28580·4	39599·1 (1)	*58·7*	39657·8 (3)			
35·6	*35·8*					
$2\,^3\mathrm{D}_3$ = 28544·8	39634·9 (4)					
$2\,^3\mathrm{P}_0'$ = 42305·59			25932·48 (2)			$2\,^3\mathrm{P} - 2\,^3\mathrm{P}'$
51·75			*51·89*			
$2\,^3\mathrm{P}_1'$ = 42253·84	25925·81 (3)	*58·56*	25984·37 (3)	*35·03*	26019·40 (3)	
119·40	*119·42*		*119·28*			
$2\,^3\mathrm{P}_2'$ = 42134·44	26045·23 (5)	*58·42*	26103·65 (3)			
$3\,^3\mathrm{P}_0'$ = 24635·3			43602·8 (1)			$2\,^3\mathrm{P} - 3\,^3\mathrm{P}'$
45·7			*45·9*			
$3\,^3\mathrm{P}_1'$ = 24589·6	43589·9 (2)	*58·8*	43648·7 (1)	*35·1*	43683·8 (3)	
126·7	*127·1*		*126·3*			
$3\,^3\mathrm{P}_2'$ = 24462·9	43717·0 (4)	*58·0*	43775·0 (2)			
$1\,^3\mathrm{P}_2'''$ = 49988·71	18191·00 (5)	*58·35*	18249·35 (2)			$2\,^3\mathrm{P} - 1\,^3\mathrm{P}'''$
−51·80	*51·79*		*51·81*			
$1\,^3\mathrm{P}_1'''$ = 49936·91	18242·79 (3)	*58·37*	18301·16 (3)	*35·25*	18336·41 (2)	
−28·05			*28·05*			
$1\,^3\mathrm{P}_0'''$ = 49908·86			18329·21 (2)			
$2\,^3\mathrm{P}_2'''$ = 28141·53	40038·0 (4)	*58·7*	40096·7 (0)			$2\,^3\mathrm{P} - 2\,^3\mathrm{P}'''$
−45·77	*45·8*		*45·9*			
$2\,^3\mathrm{P}_1'''$ = 28095·76	40083·8 (1)	*58·8*	40142·6 (2)	*34·8*	40177·4 (0)	
−25·29			*25·0*			
$2\,^3\mathrm{P}_0'''$ = 28070·47			40167·6 (1)			

Term Values.	$1\,^3\mathrm{F}_4'$ 52193·35	*81·55*	$1\,^3\mathrm{F}_3'$ 52274·90	*59·42*	$1\,^3\mathrm{F}_2'$ 52334·32	Combinations.
$2\,^3\mathrm{D}_1'$ = 36131·76					16202·56 (1)	$1\,^3\mathrm{F}' - 2\,^3\mathrm{D}'$
50·92					*50·74*	
$2\,^3\mathrm{D}_2'$ = 36080·84			16194·06 (3)	*59·2*	16253·3 (0)	
96·20			*96·3*			
$2\,^3\mathrm{D}_3'$ = 35984·64	16208·71 (4)	*81·7*	16290·4 (0)		[16349·8]	

Table III—(continued).

Term Values.	$1\,{}^3D_3$ 51353·98		$1\,{}^3D_2$ 51384·32		$1\,{}^3D_1$ 51408·36	Combinations.
		30·24		*24·04*		
$2\,{}^3D_1'$ = 36131·76			[15252]		*15274·2 (0)	
50·92						
$2\,{}^3D_2'$ = 36080·84	*15274·2 (0)		15302·7 (1)		15327·8 (0)	$1\,{}^3D - 2\,{}^3D'$
96·20						
$2\,{}^3D_3'$ = 35984·64	15368·8 (2)		15399·3 (0)			

* Used twice.

${}^3S'\ {}^3P'$ Combinations.

($1\ {}^3S_1' = 69953\cdot66$; $2\ {}^3S_1' = 35313\cdot9$.)

$1\,{}^3P_2' - 1\,{}^3S_1' = 19815\cdot71$ (8)		$1\,{}^3S_1' - 1\,{}^3P_2''' = 19965\cdot22$ (7)	
	136·35		*−51·80*
$1\,{}^3P_1' - 1\,{}^3S_1' = 19952\cdot06$ (6)		$1\,{}^3S_1' - 1\,{}^3P_1''' = 20017\cdot02$ (6)	
	31·62		*−28·02*
$1\,{}^3P_0' - 1\,{}^3S_1' = 19983\cdot68$ (2)		$1\,{}^3S_1' - 1\,{}^3P_0''' = 20045\cdot04$ (4)	
$1\,{}^3P_2' - 2\,{}^3S_1' = 54455\cdot5$ (1)			
$1\,{}^3P_1' - 2\,{}^3S_1' = 54591\cdot7$ (0)			
$1\,{}^3P_0' - 2\,{}^3S_1' = 54623\cdot6$ (00)			
$1\,{}^3S_1' - 2\,{}^3P_0' = 27647\cdot94$ (1)		$1\,{}^3S_1' - 2\,{}^3P_2''' = 41812\cdot5$ (2)	
	51·99		*−46·5*
$1\,{}^3S_1' - 2\,{}^3P_1' = 27699\cdot93$ (2)		$1\,{}^3S_1' - 2\,{}^3P_1''' = 41859\cdot0$ (1)	
	119·41		*−25·8*
$1\,{}^3S_1' - 2\,{}^3P_2' = 27819\cdot34$ (3)		$1\,{}^3S_1' - 2\,{}^3P_0''' = 41884\cdot8$ (0)	
$1\,{}^3S_1' - 3\,{}^3P_0' =$ [*]			
$1\,{}^3S_1' - 3\,{}^3P_1' = 45363\cdot6$ (1)		$1\,{}^3S_1' - 1\,{}^3D_2 = 18569\cdot0$ (0)	
	126·3		
$1\,{}^3S_1' - 3\,{}^3P_2' = 45489\cdot9$ (2)			

* Masked by a line at 45314·7 (3).

have usually been adopted, but, other things being equal, the means of the different values have been taken. Thus, in Table III the adopted values of the terms are given at the top and on the left for each combination, while the observed values are given for the corresponding lines. The agreement between the observed and calculated values is, in general, very satisfactory, except for some of the fainter lines in the far ultra-violet, where special difficulties are met with in the choice of standards, and errors of measurement are greatly magnified in conversion to wave-numbers.

Singlet Terms.

Although there are several strong lines which evidently do not form part of multiplets, the identification of the singlet terms is much more difficult and uncertain than that of the triplets, for which indications are furnished by the recurrence of separations. The expected $1\,{}^1\mathrm{P}_1'$ term, however, appears to be certainly indicated by its combinations with $1\,{}^3\mathrm{D}'_{12}$, $2\,{}^3\mathrm{P}_{012}$ and $1\,{}^3\mathrm{S}_1'$ to which attention was directed in the previous paper, namely

$$\begin{array}{lcl}
1\,{}^1\mathrm{P}_1' - 1\,{}^3\mathrm{D}_1' = 17333\cdot95\ (3) & & 1\,{}^1\mathrm{P}_1' = 89658\cdot18\\
 & \mathit{60\cdot74} & \\
1\,{}^1\mathrm{P}_1' - 1\,{}^3\mathrm{D}_2' = 17394\cdot69\ (4) & & 1\,{}^1\mathrm{P}_1' = 89658\cdot13\\
1\,{}^1\mathrm{P}_1' - 2\,{}^3\mathrm{P}_0 = 21384\cdot50\ (2) & & 1\,{}^1\mathrm{P}_1' = 89657\cdot82\\
 & \mathit{35\cdot28} & \\
1\,{}^1\mathrm{P}_1' - 2\,{}^3\mathrm{P}_1 = 21419\cdot78\ (2) & & 1\,{}^1\mathrm{P}_1' = 89657\cdot85\\
 & \mathit{58\cdot49} & \\
1\,{}^1\mathrm{P}_1' - 2\,{}^3\mathrm{P}_2 = 21478\cdot27\ (2) & & 1\,{}^1\mathrm{P}_1' = 89657\cdot82\\
1\,{}^1\mathrm{P}_1' - 1\,{}^3\mathrm{S}_1' = 19704\cdot39\ (3) & & 1\,{}^1\mathrm{P}_1' = 89657\cdot82\\
\hline
 & \text{Mean} & 1\,{}^1\mathrm{P}_1' = 89657\cdot96
\end{array}$$

The value thus deduced for $1\,{}^1\mathrm{P}_1'$ is of the expected order of magnitude (that is, not very different from $1\,{}^3\mathrm{P}$), and no other term would be appropriate to all the combinations observed.

Other singlet terms are indicated by the occurrence of certain strong pairs of lines having the separation $1\,{}^3\mathrm{P}_1' - 1\,{}^1\mathrm{P}_1'$; that is $\Delta\nu = 89905\cdot73 - 89657\cdot96 = 247\cdot77$. In association with two of these pairs there are other lines showing a separation of $237\cdot7$ from the second members of the pairs. Particulars of these lines, with the suggested singlet terms which give rise to them, are as follows :—

$$\begin{array}{ll}
\qquad\qquad (1\,{}^3\mathrm{P}_1' = 89905\cdot73) & 1\,{}^1\mathrm{P}_1' = 89657\cdot96\\
\left.\begin{array}{ll}
15422\cdot92\ (8) & = 1\,{}^1\mathrm{P}_1' - 2\,{}^1\mathrm{D}_2'\\
\qquad \mathit{247\cdot65} & \\
15670\cdot57\ (5) & = 1\,{}^3\mathrm{P}_1' - 2\,{}^1\mathrm{D}_2'
\end{array}\right\} & 2\,{}^1\mathrm{D}_2' = 74235\cdot10\\
\begin{array}{ll}
\qquad \mathit{237\cdot71} & \\
15908\cdot28\ (3) & = 1\,{}^1\mathrm{P}_1 - 1\,{}^1\mathrm{P}_1'''
\end{array} & \\
 & \\
\left.\begin{array}{ll}
25024\cdot27\ (10) & = 1\,{}^1\mathrm{P}_1' - 1\,{}^1\mathrm{P}_1\\
\qquad \mathit{247\cdot61} & \\
25271\cdot88\ (6) & = 1\,{}^3\mathrm{P}_1' - 1\,{}^1\mathrm{P}_1
\end{array}\right\} & 1\,{}^1\mathrm{P}_1 = 64633\cdot77\\
\begin{array}{ll}
\qquad \mathit{237\cdot62} & \\
25509\cdot50\ (6) & = 2\,{}^1\mathrm{D}_2' - 1\,{}^1\mathrm{P}_1'''
\end{array} & 1\,{}^1\mathrm{P}_1''' = 48725\cdot55
\end{array}$$

$$\left.\begin{array}{lcl} 29085\cdot46\ (6) & & = 1\,{}^1P_1' - 2\,{}^1S_0' \\ & \mathit{247\cdot71} & \\ 29333\cdot17\ (3) & & = 1\,{}^3P_1' - 2\,{}^1S_0' \end{array}\right\} 2\,{}^1S_0' \quad = 60572\cdot53$$

$$\left.\begin{array}{lcl} {}^{*}57213\cdot0\ \ (8) & & = 1\,{}^1S_0' - 1\,{}^3P_1' \\ & \mathit{247\cdot9} & \\ {}^{*}57460\cdot9\ \ (5) & & = 1\,{}^1S_0' - 1\,{}^1P_1' \end{array}\right\} 1\,{}^1S_0' \quad = 147118\cdot8$$

While this assignment of terms should perhaps be regarded as provisional, the correlation with the corresponding theoretical terms may be considered satisfactory. The identification of the $1\,{}^1P_1'$ term seems to be beyond question, and evidence in favour of the suggested identification of $2\,{}^1D_2'$ is afforded by its combinations with $1\,{}^3F'$ and $1\,{}^3D$. Thus

	$2\,{}^1D_2' = 74235\cdot10$	$2\,{}^1D_2' = 74235\cdot10$	$2\,{}^1D'_2 = 74235\cdot10$
	$1\,{}^3F_3' = 52274\cdot90$	$1\,{}^3F_2' = 52334\cdot32$	$1\,{}^3D_2 = 51384\cdot32$
Calcd.	21960·20	21900·78	22850·78
Obsd.	21959·82 (5*n*)	21900·74 (1*n*)	22850·74 (0)

These combinations would not be appropriate to either $1\,{}^1P_1$ or $2\,{}^1S_0'$, which belong to the same group of levels arising from the electron configuration $(2_2\,3_2)$. It will be observed that the suggested $2\,{}^1D_2'$ term is larger than either of the $1\,{}^3D'$ or $2\,{}^3P$ terms of the same group, and would accordingly not follow the more general rule that a term of greatest multiplicity is the deepest of a group. Extrapolation by a Rydberg table gives $1\,{}^1D_2'$ about 214,000, while the extrapolated value of $1\,{}^3P$ is considerably smaller. There are, however, theoretical reasons for supposing that $1\,{}^3P$ must be the deepest term of the spectrum, and it is probable that these simple extrapolations do not lead to the correct relative values of the deepest terms. A small negative correcting term (say, $0\cdot012/m$) in the formula for ${}^1D_2'$, and a somewhat larger negative term (say, $0\cdot236/m$) in that for ${}^3P$, would suffice to make both $1\,{}^3P$ and $1\,{}^1D_2'$ larger than 214000, with $1\,{}^3P > 1\,{}^3D'$. There would be nothing unusual in such correcting terms, but, as already pointed out, the question as to which is actually the deepest term of the spectrum cannot be settled until more detailed observations have been made in the region beyond λ 830.

In the assignment of the $1\,{}^1P_1$ and $2\,{}^1S_0'$ terms, Hund's rule for the deeper term was applied in the first instance. Adopting $2\,{}^1S_0' = 60572\cdot5$, a simple Rydberg extrapolation gives $1\,{}^1S_0' = 146060$, which at once indicates the strong pair of lines at 57213·0, 57460·9 as $1\,{}^1S_0' - 1\,{}^3P_1'$ and $1\,{}^1S_0' - 1\,{}^1P_1'$ respectively. The ${}^1S_0'$ terms may accordingly be represented by the formula

---

* From Bowen and Ingram's measures.

$$m\,{}^1S_0' = 4R/[m + 0\cdot655626 + 0\cdot071230/m]^2$$

which is again remarkable for the small value of the correcting term. Extrapolation by this formula gives $3\,{}^1S_0' = 32406\cdot6$, but the corresponding combinations with $1\,{}^1P_1'$ and $1\,{}^3P_1'$ have not been found.

So far as the above observed combinations are involved, $2\,{}^1S_0'$ might have been interchanged with $1\,{}^1P_1$. But if $1\,{}^1P_1$ (= 64634) were to be taken as $2\,{}^1S_0'$, the extrapolated value of the deepest term of this type would be about 170000, and a pair of lines with separation 247·7 would have been expected in the region about ν 80000. The fact that no such lines have been observed, although well within the range of observation, is strong evidence that the $2\,{}^1S_0'$ and $1\,{}^1P_1$ terms have been correctly allocated.

The $1\,{}^1P'''$ term indicated above has been chosen as such in consideration of its appropriate magnitude.

Attention should be directed to the fact that in the above scheme, some of the combinations which are possible according to the familiar selection rules do not appear in the spectrum. Thus, there are no indications of $1\,{}^3P_2' - 2\,{}^1D_2'$, or of $1\,{}^3P_0' - 1\,{}^1P_1$, $1\,{}^3P_2' - 1\,{}^1P_1$. Corresponding lines in the analogous spectrum of Si I are also weak or missing. While this may throw some doubt on the identification of the singlet terms in question, there is apparently no other evidence of the existence of such terms as theory indicates.

Other combinations involving singlet terms already mentioned are as follows:

$$1\,{}^3S_1' - 1\,{}^1P_1''' = 21227\cdot98\ (1)$$
$$1\,{}^1P_1 - 1\,{}^1P_1''' = 15908\cdot28\ (3)$$

Additional combinations were identified by trial of extrapolated values, namely

$$\left.\begin{array}{l} 2\,{}^1S_0' - 2\,{}^1P_1' = 19585\cdot30\ (2)\\ 2\,{}^1D_2' - 2\,{}^1P_1' = 33247\cdot67\ (7)\\ 1\,{}^1P_1 - 2\,{}^1P_1' = 23646\cdot16\ (3)\end{array}\right\} 2\,{}^1P_1' = 40987\cdot42$$

Two other possible combinations, suggested by a consideration of the probable magnitudes of the $1\,{}^1F_3'$ and $1\,{}^1D_2$ terms are as follows:—

$2\,{}^1D_2' - 1\,{}^1F_3' = 22067\cdot08\ (5)$ $\quad 1\,{}^1F_3' = 52168\cdot02$?

$2\,{}^1D_2' - 1\,{}^1D_2 = 22480\cdot60\ (10)$ $\quad 1\,{}^1D_2 = 51754\cdot50$?

Numerous singlets remain unidentified.

Double Electron Transitions.

Groups of lines, or multiplets, have been found in which the separations have nothing in common with those of the terms already considered. It does not seem possible that these can form part of the theoretical scheme of terms due to the changing orbit of a single electron, and it is probable that they are to be attributed to simultaneous transitions of two electrons. The theoretical predictions for some of the terms which may arise in this way are shown in Table IV.

Table IV.—Predicted Terms for Double Transitions.

K 1_1	L $2_1\ 2_2$	M 3_1	 3_2	 3_3	N 4_1		Terms.	Estimated relative values.
2	2	2				$(3_1\,3_1)$	$a\,{}^1S'$	0
2	2	1	1			$(3_1\,3_2)$	$a\,{}^3P'$, $a\,{}^1P'$	− 20000
2	2	1		1		$(3_1\,3_3)$	$a\,{}^3D'$, $a\,{}^1D'$	− 42000
2	2	1			1	$(3_1\,4_1)$	$b\,{}^1S'$, $a\,{}^3S'$	− 50000
2	2		2			$(3_2\,3_2)$	$a\,{}^3P$, $a\,{}^1D'''$, $a\,{}^1S'''$	− 42000
2	2		1	1		$(3_2\,3_3)$	$a\,{}^3F'$, $a\,{}^3D$, $a\,{}^3P'''$, $a\,{}^1F'$, $a\,{}^1D$, $a\,{}^1P'''$	− 64000
2	2			2		$(3_3\,3_3)$	$a\,{}^3F$, $a\,{}^3P''$, $a\,{}^1G'$, $a\,{}^1D'''''$, $a\,{}^1S'''''$	− 86000

The terms are dashed or undashed so as to conform with the selection rules for possible combinations with the terms of Table II. The first term of each class is indicated by the prefix *a* and the second by *b*. $a\,{}^1S'$, $a\,{}^1S'''$ and $a\,{}^1S'''''$, for example, are the first of three different sequences of ${}^1S'$ terms, while $a\,{}^1S'$, $b\,{}^1S'$ are successive members of the same sequence.

As no intercombinations with the previous set of terms have been found, the values of the above terms cannot yet be stated with any precision. Roughly approximate estimates of the differences between the different groups, however, may possibly be deduced from the values of the terms already known, and such estimates may be of use in indicating the parts of the spectrum in which combination groups of lines may be expected. For example, as shown in Table II, the configuration $2_2\,3_3$ gives the $1\,{}^3D'$ group of terms, while $2_2\,3_2$ gives the group beginning with $1\,{}^3F'$; so that, taking rough means, the work required to convert the 3_2 electron to 3_3 is represented by $70{,}000 - 50{,}000 = 20{,}000$. Similarly, referring to Table IV, the configurations $3_1\,3_2$ and $3_1\,3_3$ give the $a\,{}^3P'$ and $a\,{}^3D'$ groups respectively, and if the work required for the change from 3_2 to 3_3

were the same as in the previous case, we should have $a\,{}^3\mathrm{P}' - a\,{}^3\mathrm{D}'$ of the order of 20000. On account of the reduced screening effect of the 3_1 electron as compared with the 2_2, however, this difference would be increased, say to 22000. Other differences for the term groups have been estimated in a similar manner.

In view of the uncertainty with regard to the $1\,{}^3\mathrm{P}$ term, no attempt has been made to estimate the actual values of the double-transition terms. The estimated *relative* values given in the last column of Table IV are accordingly referred to $a\,{}^1\mathrm{S}'$ taken as zero. These will serve equally well in attempts to correlate observed multiplets with the theoretical terms. [Bowen's value for $1\,{}^3\mathrm{P}$ (see Addendum) suggests that $a\,{}^1\mathrm{S}'$ may be of the order of − 80000.]

Three multiplets which are inter-related are shown in Table V, with the types of terms suggested by the above considerations. Besides these, there is a fairly strong isolated multiplet of rather nebulous lines beginning at λ 2897 ($\nu = 34502$), and probably another beginning at λ 4073 ($\nu = 24544$); these have been named *A* and *B* respectively for convenience of reference.

Table V.—Double Transition Multiplets.

	$a\,{}^3\mathrm{P}_0'$ −25759·10	*56·23*	$a\,{}^3\mathrm{P}_1'$ −25815·13	*70·63*	$a\,{}^3\mathrm{P}_2'$ −25885·74
$a\,{}^3\mathrm{S}_1'$ = −50000·00*	24240·90 (1)	*56·03*	24184·87 (2)	*70·61*	24114·26 (3)

* Assumed relative value.

	$a\,{}^3\mathrm{D}_3'$ −43946·53	*53·89*	$a\,{}^3\mathrm{D}_2'$ −43892·64	*43·13*	$a{}^3\mathrm{D}_1'$ −43849·51
$a\,{}^3\mathrm{P}_0'$ = −25759·10					18090·41 (2)
56·23					*56·23*
$a\,{}^3\mathrm{P}_1'$ = −25815·13			18077·29 (4)	*43·11*	18034·18 (3)
70·63			*70·59*		*70·67*
$a\,{}^3\mathrm{P}_2'$ = −25885·74	18060·57 (5)	*53·87*	18006·70 (3)	*43·19*	17963·51 (0)
$a\,{}^3\mathrm{F}_2'$ = −63173·80	19227·17 (00)	*53·99*	19281·16 (2)	*43·23*	19324·39 (2)
33·73	*33·74*		*33·82*		
$a\,{}^3\mathrm{F}_3'$ = −63207·53	19260·91 (2)	*54·07*	19314·98 (3)		
40·52	*40·61*				
$a\,{}^3\mathrm{F}_4'$ = −63248·05	19301·52 (5)				

Multiplet A.

34648·9 (6)				
91·1				
34557·8 (4)	*157·5*	34715·3 (4)		
55·3		*54·4*		
34502·5 (3)	*158·4*	34660·9 (2)	*79·4*	34740·3 (2)

Table V—(continued).

Multiplet B.

24737·39 (5)				
192·59				
24544·80 (2)	*230·82*	24775·62 (4)		
		51·77		
		24723·85 (3)	*107·17*	24831·03 (3)

ADDENDUM.

Since the foregoing account of our work was completed, an important paper on the extreme ultra-violet spectra of carbon, nitrogen, oxygen, and fluorine has been published by S. I. Bowen, of Prof. Millikan's Laboratory, at Pasadena.* The work of Dr. Bowen is remarkable for the high resolution and precision of wave-lengths which have been attained in this difficult region, and for the classification of many of the lines of the elements in question at different stages of ionisation. In the case of N II, Dr. Bowen has amended the values of the 1 ^{3}P′ terms (3 *k* P in his notation), and thence of some of the remaining terms, in the manner already explained in the present communication, and has identified the deep 1 ^{3}P (*a* P) terms through their combination with 1 ^{3}P′. Thus, adopting the values of 1 ^{3}P′ from Table II, in place of 93000 assigned to 1 $^3P_2$ by Bowen, the multiplet 1 ^{3}P — 1 ^{3}P′ is as follows :—

Bowen's *a* P→		1 $^3P_2$ 238716	*84*	1 $^3P_1$ 238800	*50*	1 $^3P_0$ 238850
Bowen's 3 *k* P	1 $^3P_0'$ = 89937·3			148858 (2)		
	31·6			*29*		
	1 $^3P_1'$ = 89905·7	148804 (2)	*83*	148887 (1)		*148943 (3)
	136·3	*139*		*138*		
	1 $^3P_2'$ = 89769·4	*148943 (3)		149025 (2)		

* Used twice.

The term 1 ^{3}P is thus shown to be greater than 210000, as we had anticipated, and although somewhat greater than expected, there can be little doubt that the term has been correctly identified. As already pointed out, the triplet 1 ^{3}P — 1 ^{1}P′ would also be expected near the above multiplet, but this does not appear in Bowen's list, which, however, only includes lines classified by him.

In the discussion of his observations, Bowen has shown the importance of a group of terms which arises when one of the 2_1 electrons is displaced to a 2_2 orbit ; that is (omitting the K electrons), from the configuration (2_1) $(2_2)^3$, or

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* 'Phys. Rev.,' vol. 29, p. 231 (Feb. 1927).

sp^3 in the notation adopted by Bowen. For this configuration the theoretical terms, distinguished by the prefix *b*, are

$$^1P,\quad ^1D,\quad ^3S,\quad ^3P,\quad ^3D,\quad ^5S,$$

or, in the notation of the present paper,

$$^1P_1',\quad ^1D,\quad ^3S,\quad ^3P',\quad ^3D,\quad ^5S.$$

To avoid confusion, the prefix *b* of Bowen will be replaced by β.

In addition to the combinations given by Bowen, a few others have been noted among the lines occurring in our list (Table I). One of them provides an interesting check on the values of the $\beta\,{}^3D$ terms, and thence of $1\,{}^3P$. One of Bowen's multiplets may be constructed as follows, wave-numbers in square brackets being calculated from the known separations of the $2\,{}^3P$ terms of Table II :—

Bowen's *b* D→		$\beta\,{}^3D_1$ 146597·8		$\beta\,{}^3D_2$ 146597·0	*−10·4*	$\beta\,{}^3D_3$ 146607·4
Bowen's 3 *m* P	$2\,{}^3P_0$ = 68273·3	78324·5 (2)				
	35·2	*[35·2]*				
	$2\,{}^3P_1$ = 68238·1	[78359·7]	[0·8]	78358·9 (3)		
	58·4	*[58·4]*		*[58·4]*		
	$2\,{}^3P_2$ = 68179·7	[78418·1]	[0·8]	[78417·3]	[−10·4]	78427·7 (4)

An additional multiplet from our own list of lines, taking values of $1\,{}^3D'$ from Table II, may similarly be represented as follows :—

	$\beta\,{}^3D_1$ 146595·8	*−0·5*	$\beta\,{}^3D_2$ 146596·3	*−10·6*	$\beta\,{}^3D_3$ 146606·9
$1\,{}^3D_1'$ = 72324·2	74271·6 (1)	[−0·5]	[74272·1]		
60·8	*[60·8]*		*[60·8]*		
$1\,{}^3D_2'$ = 72263·4	[74332·4]	[−0·5]	74332·9 (2)	[−10·6]	[74343·5]
96·2			*[96·2]*		*[96·2]*
$1\,{}^3D_3'$ = 72167·2			[74429·1]	[−10·6]	74439·7 (3)

It will be seen that there is a close agreement between the two sets of values of $\beta\,{}^3D$, and the mean values may accordingly be adopted, namely :—

$$\left.\begin{aligned}\beta\,{}^3D_1 &= 146596{\cdot}8\\ \beta\,{}^3D_2 &= 146596{\cdot}7\end{aligned}\right\}\text{Not resolved}$$

$$\qquad\qquad\mathit{-10{\cdot}5}$$

$$\beta\,{}^3D_3 = 146607{\cdot}2$$

These terms may next be used to obtain another set of values of $1\,{}^3P_{012}$

through the combination $1\,^3P - \beta\,^3D$. Using Bowen's wave-numbers, with which our measures are in good agreement, the multiplet is as follows :—

Bowen's *b* D→			$\beta\,^3D_1$		$\beta\,^3D_2$		$\beta\,^3D_3$
			146596·7	*0*	146596·7	*−10·5*	146607·2
Bowen's *a* P	$1\,^3P_0$ =	238849·1	92252·4 (6)				
		49·6	*[49·6]*				
	$1\,^3P_1$ =	238799·5	[92202·8]		92202·8 (7)		
		84·3	*[84·3]*		*82·7*		
	$1\,^3P_2$ =	238715·2	[92120·1]		92120·1 (3)	*−13·7*	92106·4 (8)

The values of $1\,^3P$ thus obtained are in striking agreement with those derived directly from $1\,^3P - 1\,^3P'$ and clearly indicate the great accuracy of Bowen's measures.

Other combinations given by Bowen, using mean values for $1\,^3P$, are as follows :—

Bowen's *a* P→		$1\,^3P_2$		1^3P_1		$1\,^3P_0$
		238715·6	*84·1*	238799·7	*49·8*	238849·5
Bowen's *b* S; $\beta\,^3S_1$ =	83721·4	154995·5 (5)	*82·7*	155078·2 (5)	*48·8*	155127·0 (4)
Bowen's 3 *n* D: $1\,^3D_1$ =	51408·4	[187307·2]		[187391·3]		[187441·1]
$1\,^3D_2$ =	51384·3	[187331·3]		[187415·4]		
$1\,^3D_3$ =	51354·0	[187361·6]				
Observed		187368 (3)		187431 (3)		

The agreement between the calculated and observed values of $1\,^3P - 1\,^3D$ is as good as can be expected in this part of the spectrum, where 1 Ångström unit represents about 360 units of wave-number.

Another multiplet indicated by Bowen represents the combination $1\,^3P - \beta\,^3P'$. This involves the group of lines about λ 916, in which our own photographs of the N II spectrum fail to show Bowen's line at λ 916·698 (8) ($\nu = 109087{\cdot}2$). Bowen's classification of this group may be represented as follows :

Bowen's *a* P→		$1\,^3P_2$ *		$1\,^3P_1$		$1\,^3P_0$
		238715·6	*84·1*	238799·7	*49·8*	238849·5
Bowen's *b* P: $\beta\,^3P_0'$ =	129625·0			109174·7 (6)		
	−5·6			*6·5*		
$\beta\,^3P_{12}'$ =	129630·6	109087·2 (8)	*81·0*	109168·2 (6)	*49·4*	109217·6 (6)

The absence of the line 109087 from our N II spectrum throws considerable doubt on this identification of the β $^3P'$ terms, but some support is afforded by other combinations apparently involving β $^3P'$ which are not included in Bowen's list, namely :—

	$\beta\,^3P_0'$ 129625·0	−5·6	$\beta\,^3P_{12}'$ 129630·6
$2\,^3P_0$ = 68273·3			[61357·3] 61355·0 (0)
$2\,^3P_1$ = 68238·1	[61386·9]		[61392·5]
		61386·6 (1)	
$2\,^3P_2$ = 68179·7			[61450·9] 61447·0 (1)
$1\,^3S_1'$ = 69953·7	[59671·3]		[59676·9]
		59671·9 (5)	
$1\,^3D_1'$ = 72324·2	[57300·8]*		[57306·4]*
$1\,^3D_2'$ = 72263·4			[57367·2] 57365·1 (2)
$1\,^3D_3'$ = 72167·3			[57463·3]†

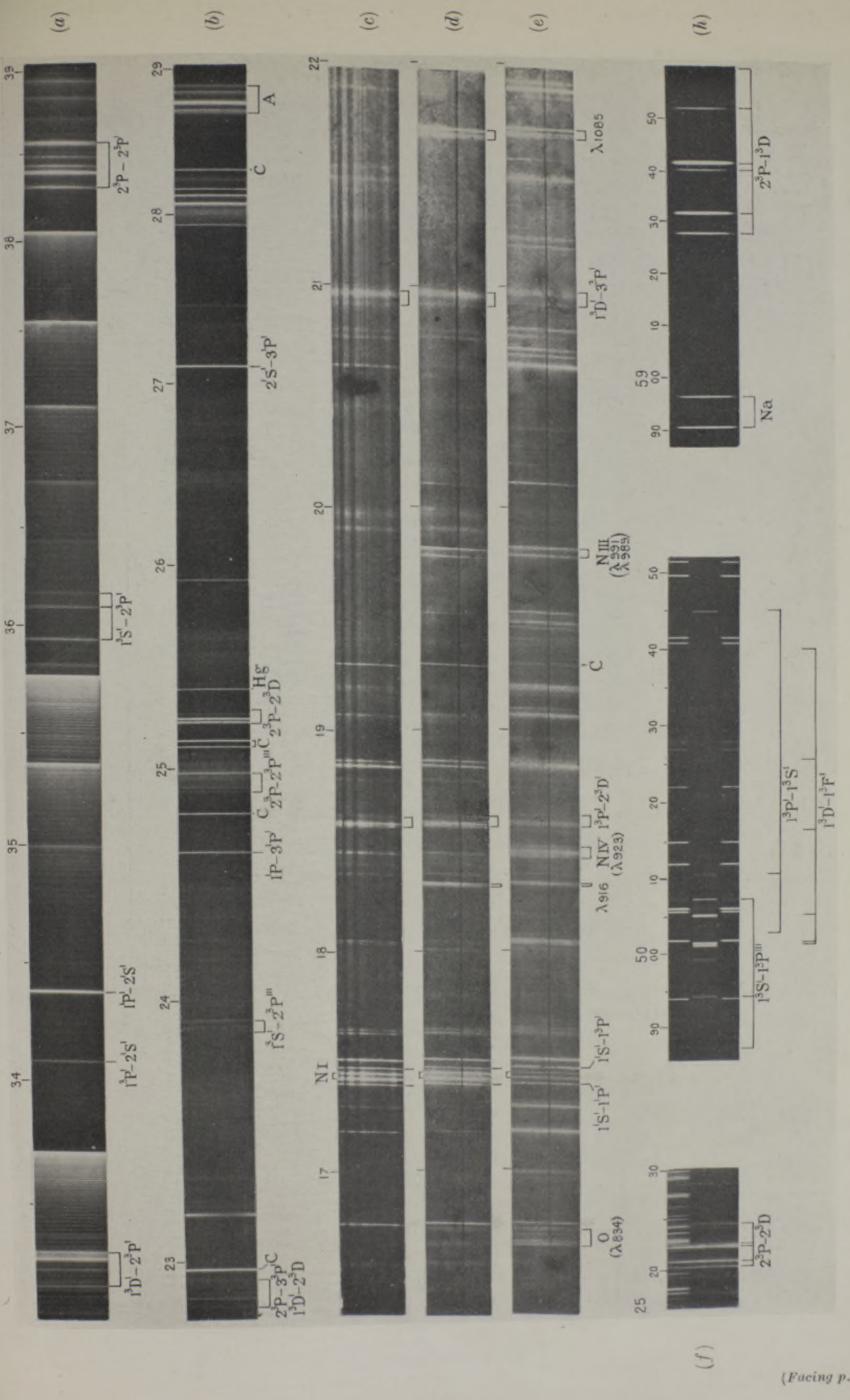
* Masked by N I 57298·1.
† Masked by N II 57460·9.

The calculated wave-numbers of possible lines are enclosed in square brackets, and it will be seen that there is a fair agreement with the observed values. It should be noted, however, that a singlet term, which might be β $^1P_1'$, would represent the observations almost equally well. Observations of these lines in higher orders of the grating will probably throw further light on the characters of the above multiplets.

Summary.

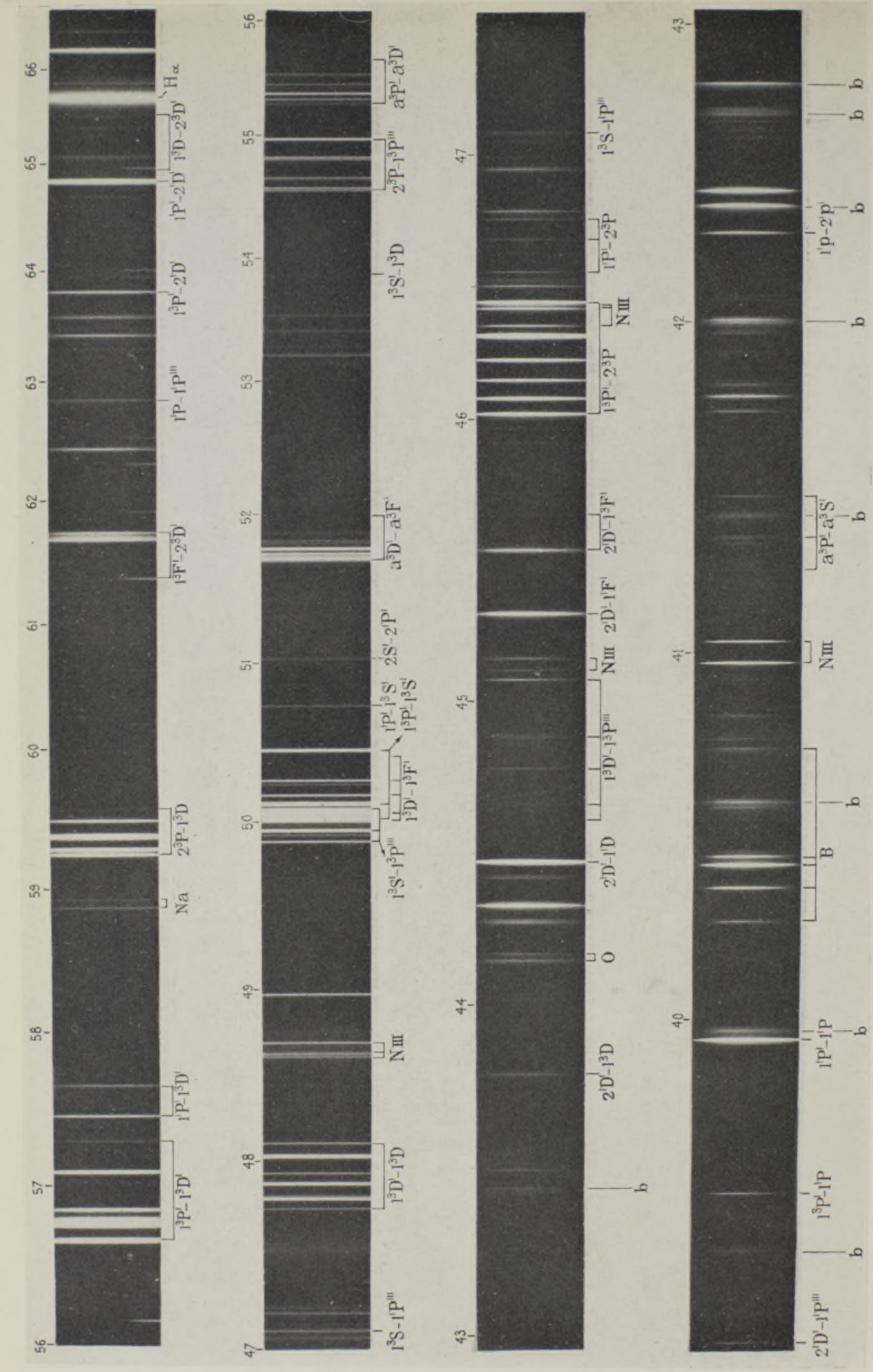
In continuation of a previous investigation of the spectrum of ionised nitrogen (N II), observations have been made over the range λ 6836 to λ 830. Of 340 lines recorded in this region, about one-half have now been classified ; and of the remaining lines more than 100 are very faint. The spectrum is built up from triplet and singlet terms, the absolute values of which have been determined with the aid of a sequence of three $^3P' - {}^3P$ multiplets.

The scheme of terms deduced from the Heisenberg-Hund theory of complex spectra has greatly facilitated the analysis of the spectrum, and the results are in excellent agreement with the theory. Of the 19 deepest terms predicted by the theory for transitions of a single electron, complex terms being counted



Spectra of Nitrogen.

(*Facing p.* 688.)



Spectra of Nitrogen.

as one, all but one have been identified. The term 1^3P_0 recently identified by Bowen from a multiplet at λ 671, is probably the deepest, its value being 238850, corresponding to an ionisation potential of 29·5 volts.

A few multiplets which appear in the spectrum are attributed to double electron transitions.

The authors are indebted to Mr. E. W. H. Selwyn for some excellent photographs taken with the vacuum spectrograph, and to Mr. R. H. Fowler and Mr. D. R. Hartree for valuable guidance on certain theoretical questions.

DESCRIPTION OF PLATES 47 and 48.

Plate 47.—This is intended to give a general view of the spectrum of N II between λ 6600 and λ 3900. The photographs were taken with a glass spectrograph of moderate dispersion. It should be noted that the short lines at the bottom of the first strip represent a comparison spectrum of iron. Lines due to N III or to a slight impurity of oyxgen are indicated, as are also the weak bands due to nitrogen (*b*).

Plate 48.—(*a*, *b*) Nitrogen vacuum tube, quartz spectrograph, λ 3900—λ 2300. Weak discharge, favouring development of N II. (*c*) Nitrogen tube, vacuum spectrograph, λ 2200–λ 1650 ; 1st order only. Shows some lines of N III in addition to the lines of N II. (*d*) Nitrogen tube, λ 2200–λ 1650 in 1st order, and λ 1100–λ 825 in 2nd order. (*e*) Same as (*d*), but with stronger discharge. (*f*) Enlargement of $2\,^3P - 2\,^3D$ group λ 2520–λ 2524. (*g*) Group at λ 5007, 3rd order 10-feet concave grating, showing resolution of λ 5001. (*h*) Enlargement of $2\,^3P - 1\,^3D$ group, λ 5928–λ 5961, 1st order 10-feet grating.

The Spectrum of Doubly Ionised Oxygen (*O III*).

By A. Fowler, D.Sc., F.R.S., Yarrow Research Professor of the Royal Society,
Imperial College, South Kensington.

(Received November 4, 1927.)

Introductory.

In continuation of previous investigations of the spectra of the lighter elements, the present paper gives an account of the spectrum of doubly ionised oxygen. The lines have been observed mainly with suitably strong discharges in vacuum tubes, and have been distinguished from those of O II by the usual method of comparing the intensities of the lines under the action of different discharges. Most of the stronger lines have been measured with considerable accuracy on plates taken with a 10-ft. concave grating, or with a large quartz spectrograph. As was expected, the spectrum is generally similar to that of N II,* and the terms so far determined are in entire accordance with Hund's theory.

Notation.

It has been found that the system of numeration used for the terms of N II is not conveniently adaptable to certain other spectra, and in the present communication a modified form which seems likely to be of more general application, has been adopted. In particular, it has seemed desirable to assign the same prefix to all terms which arise from the same electron configuration. A convenient procedure, which has already been followed to some extent by others, is to use the orbital designation of the "series electron" as a prefix, with small italic letters for electron orbits, as distinct from the capital letters used for terms. Thus, $3s\,{}^3P_2$ will indicate that the ^3P term in question is due to a configuration in which the series electron occupies a 3_1 orbit. Combination possibilities are then shown by the application of the ordinary selection rule for azimuthal quantum numbers to the electron symbols, in addition to the inner quantum number rule applicable to the term symbols. For example, a $2s\,{}^1P_1$ might combine with a $3p\,{}^1P_1$, but not with a $3s\,{}^1P_1$ or $3d\,{}^1D_2$ term. In this way it becomes unnecessary to "dash" any of the term or electron symbols in connection with the simpler spectra.

For complex spectra, combination possibilities can be sufficiently indicated by assigning undashed electron symbols to the principal family of terms, and dashed symbols to other families, in accordance with the rules for electron transitions ($\Delta k = \pm 1$ for one electron and $\Delta k = 0$ or 2 for a second). When there are more than two families of terms, they may be distinguished by additional dashes to the electron symbols, an even number for what would otherwise be undashed terms, and an odd number for the remainder, in accordance with previous usage.

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* A. Fowler and L. J. Freeman, 'Roy. Soc. Proc.,' A, vol. 114, p. 662 (1927).

When different sets of terms arise from a given configuration, but with different states of the ion or "core," terms of similar type in the same group may be distinguished by arbitrary numerical superscripts applied to the *term* symbols. For example, in the spectrum of O II there are three $3d\,^2D$ terms, each based upon a different state of the O III core, which may be ^3P, ^1D, or ^1S; these may be distinguished by retaining $3d\,^2D$ for the term based upon ^3P (the deepest term of O III), and writing $3d\,^2D^1$, $3d\,^2D^2$ for the others. Such superscripts, of course, are not connected in any way with the combination properties of the terms.

Rydberg sequences are naturally shown by such a succession of terms, for example, as $2s\,^1P$, $3s\,^1P$, $4s\,^1P$.

Predicted Terms of O III.

The spectrum of O III may be considered as arising from the addition of an electron to an O IV core, which has five external electrons. This core is normally in the ^2P state (like the neutral atom of boron), and the addition of another electron generates a family of singlet and triplet terms, as shown in Table I. The prefixes for these terms, as already explained, are $2p$, $3s$, and so on.

Table I.—Predicted Terms of O III.

K	L		M			N				Terms.
1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2			
2	2	1						$s^2 p$		[^{2}P] O IV core.
2	2	2						$s^2 p^2$	$2p$	^{3}P ^{1}D ^{1}S
2	2	1	1					$s^2 p . s$	$3s$	^{3}P ^{1}P
2	2	1		1				$s^2 p . p$	$3p$	^{3}D ^{3}P ^{3}S ^{1}D ^{1}P ^{1}S
2	2	1			1			$s^2 p . d$	$3d$	^{3}F ^{3}D ^{3}P ^{1}F ^{1}D ^{1}P
2	2	1				1		$s^2 p . s$	$4s$	^{3}P ^{1}P
2	2	1					1	$s^2 p . p$	$4p$	^{3}D ^{3}P ^{3}S ^{1}D ^{1}P ^{1}S
2	1	2						$s\,p^2$		[^{4}P ^{2}D ^{2}P ^{2}S]. O IV core.
2	1	3						$s\,p^3$	$2p'$	^{5}S ^{3}D ^{3}P ^{3}S ^{1}D ^{1}P Other quintet, triplet and singlet terms.

There is a second family of terms, depending upon a state of the O IV core, in which one of the 2_1 electrons has already been displaced to a 2_2 orbit. This configuration (of O IV) yields the terms ^{4}P, ^{2}D, ^{2}P, ^{2}S, of which the first is the deepest, and the addition of the sixth electron gives rise to quintet, triplet, and singlet terms. These may be distinguished from terms of the first family by dashing the electron symbols, and intercombinations may then occur in accordance with the usual rules for dashed terms. The deepest of the terms of this second family are indicated in the last row of Table I.

In Table I the electron configurations are shown in two different ways, the first of which needs no explanation. The second (column 5) is a convenient way of summarising the configuration which has been used by Russell and others. The two K, or 1_1, electrons being disregarded, since they do not contribute to the spectroscopic terms, the configuration of the electrons in uncompleted shells is indicated by writing s for n_1, p for n_2, and so on, the number of electrons of each type being shown by an appropriate superscript. When an electron is in an excited state, the corresponding orbit symbol is separated from the others by a dot. Thus $s^2\,p\,.\,s$, in the table, means that two of the electrons in the uncompleted L shell are in 2_1 orbits, one in 2_2, and the last in an excited n_1 orbit.

Term Values.

The occurrence of triplets and multiplets made it comparatively easy to trace many of the triplet terms, and approximate values were assigned to them, in the first instance, by the application of a simple Rydberg formula to the two ^{3}S terms which were early recognised. While the present work was awaiting the identification of singlet terms, most of the triplet terms and combinations were independently discovered and published by C. Mihul,* in complete agreement with the writer's results. Credit is solely due to M. Mihul, however, for the first identification of quintet terms.

Intercombinations between singlet and triplet terms are much less conspicuous than in the corresponding spectrum of N II, and were not very readily identified. A beginning was eventually made with the following pairs of lines, having separations already known in connection with triplet terms :—

$$\left.\begin{array}{l} 3p\,{}^3\mathrm{D}_1 - 3d\,{}^1\mathrm{P}_1 = 30868\cdot95\ (5) \\ 3p\,{}^3\mathrm{D}_2 - 3d\,{}^1\mathrm{P}_1 = 30732\cdot62\ (3) \end{array}\right. \quad \Delta\nu = 136\cdot32$$

$$\left.\begin{array}{l} 3d\,{}^1\mathrm{P}_1 - 4p\,{}^3\mathrm{D}_1 = 41752\cdot5\ (5) \\ 3d\,{}^1\mathrm{P}_1 - 4p\,{}^3\mathrm{D}_2 = 41859\cdot8\ (1) \end{array}\right. \quad \Delta\nu = 107\cdot2.$$

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* 'Comptes Rendus,' vol. 183, p. 1035 (1926); vol. 184, pp. 89, 874, 1055 (1927).

With the values of the triplet terms previously determined, these gave very closely accordant values for $3d\,^1P_1$, and there could be little doubt that the identification was correct. Using the finally adopted values for the triplet terms (Table II), it results that

$$3d\,^1P_1 = 119859 \cdot 28.$$

Next, by comparison with N II, it seemed probable that $3p\,^1D_2$ would be somewhat greater than $3p\,^3D$, and it was accordingly estimated that a strong combination with $3d\,^1P_1$ would be found in a position $\nu > 31000$. The line 33777·60 (6) led to a value for $3p\,^1D_2$ which was subsequently justified by other appropriate combinations, including a very faint line representing an intercombination. Thus :—

$$\begin{array}{lll} 3d\,^1P_1 & = & 119859 \cdot 28 \\ & & \;\;33777 \cdot 60\ (6) \\ \hline 3p\,^1D_2 & = & 153636 \cdot 88 \\ \hline \end{array} \qquad \begin{array}{lll} 3s\,^3P_1 & = & 177217 \cdot 85 \\ 3p\,^1D_2 & = & 153636 \cdot 88 \\ \hline & & \;\;23580 \cdot 97 \\ \text{Observed} & & \;\;23581 \cdot 1\ (00) \\ \hline \end{array}$$

The term $3p\,^1D_2$ should combine with $3s\,^1P_1$, giving a strong line of wave-number less than $3s\,^3P - 3p\,^1D_2$; *i.e.* < 23300. The only suitable line appears to be 17876·55 (6), and, adopting this, the value of $3s\,^1P_1$ is found as follows :—

$$\begin{array}{lll} 3p\,^1D_2 & = & 153636 \cdot 88 \\ & & \;\;17876 \cdot 55\ (6) \\ \hline 3s\,^1P_1 & = & 171513 \cdot 43 \\ \hline \end{array}$$

This in turn would be expected to combine with $3p\,^1S_0$, and the most probable representative is 25235·34 (8), giving

$$3p\,^1S_0 = 146278 \cdot 09.$$

Other singlet terms were provisionally identified in a similar manner by the selection of lines which led to values of appropriate magnitude for them. Confirmatory combinations were found in some cases, and a general confirmation is afforded by comparison with the terms of N II.

An important contribution to the investigation has been made by I. S. Bowen* by the classification of six singlets of O III observed by him in the extreme ultra-violet, namely,

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* 'Phys. Rev.,' vol. 29, p. 241 (1927).

Bowen		λ	ν	Δ ν
$a\mathrm{S} - b\mathrm{P}$	$2p\,{}^1\mathrm{S}_0 - 2p'\,{}^1\mathrm{P}_1$	597·82 (4)	167274	22916
$a\mathrm{D} - b\mathrm{P}$	$2p\,{}^1\mathrm{D}_2 - 2p'\,{}^1\mathrm{P}_1$	525·79 (6)	190190	
$a\mathrm{S} - 3k\mathrm{P}$	$2p\,{}^1\mathrm{S}_0 - 3s\,{}^1\mathrm{P}_1$	434·91 (2)	229933	22899
$a\mathrm{D} - 3k\mathrm{P}$	$2p\,{}^1\mathrm{D}_2 - 3s\,{}^1\mathrm{P}_1$	395·52 (2)	252832	
$a\mathrm{S} - 3n\mathrm{P}$	$2p\,{}^1\mathrm{S}_0 - 3d\,{}^1\mathrm{P}_1$	355·06 (0)	281643	22919
$a\mathrm{D} - 3n\mathrm{P}$	$2p\,{}^1\mathrm{D}_2 - 3d\,{}^1\mathrm{P}_1$	328·34 (0)	304562	

Bowen did not assign values to any of these terms, but $3s\,{}^1\mathrm{P}_1$ and $3d\,{}^1\mathrm{P}_1$ having now been identified, the values of $2p\,{}^1\mathrm{D}_2$, $2p\,{}^1\mathrm{S}_0$ and $2p'\,{}^1\mathrm{P}_1$ can be determined. It thus seems probable that the most accurate term values for the whole spectrum will be yielded by the sequence of three $p\,{}^1\mathrm{D}_2$ terms. These are represented with fair approximation by a simple Rydberg formula, but more accurately by the formula

$$p\,{}^1\mathrm{D}_2 = 9\mathrm{R}/[m + 0{\cdot}545336 - 0{\cdot}019824/m]^2, \quad \mathrm{R} = 109737, \quad m = 1, 2, 3.$$

This gives

$$2p\,{}^1\mathrm{D}_2 = 424385, \quad 3p\,{}^1\mathrm{D}_2 = 153637, \quad 4p\,{}^1\mathrm{D}_2 = 78869.$$

As the correcting term is so small, these values are unlikely to be much in error. They agree closely with those adopted in the first instance by the application of a simple Rydberg formula to the two ${}^3\mathrm{S}$ terms.

The $2p\,{}^3\mathrm{P}$ terms were derived in the first instance from the unresolved lines λ 374·3 and λ 305·7, indicated by Bowen as probably representing the combinations of these terms with $3d\,{}^3\mathrm{P}$ and $3d\,{}^3\mathrm{D}$ respectively. If the unresolved lines be taken as the strongest components of the resulting multiplets, we have

	λ	ν	
$2p\,{}^3\mathrm{P}_2 - 3s\,{}^3\mathrm{P}_2 =$	374·3	267165;	$3s\,{}^3\mathrm{P}_2 = 176961$, $2p\,{}^3\mathrm{P}_2 = 444126$,
$2p\,{}^3\mathrm{P}_2 - 3d\,{}^3\mathrm{D}_3 =$	305·7	327118;	$3d\,{}^3\mathrm{D}_3 = 117243$, $2p\,{}^3\mathrm{P}_2 = 444361$.

The value of $2p\,{}^3\mathrm{P}_2$ thus indicated is about 20,000 units greater than that of $2p\,{}^1\mathrm{D}_2$, in good agreement with the theoretical estimate of Fowler (R. H.) and Hartree,* and the identifications of the lines in question are probably correct.

The separations $2p\,{}^3\mathrm{P}_0 - 2p\,{}^3\mathrm{P}_1 = 116$, and $2p\,{}^3\mathrm{P}_1 - 2p\,{}^3\mathrm{P}_2 = 193$, are given with considerable accuracy by combinations between these terms and those of the second family ($2p'$ terms), the values of which naturally follow in correct relation to those of the first family. Further support for the above identifications is afforded by the probable combinations $2p'\,{}^3\mathrm{P} - 3p\,{}^3\mathrm{D}$ (λ 658·4) and $2p\,{}^3\mathrm{P} - 3d\,{}^3\mathrm{P}$ (λ 303·7) noted during the present investigation.

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* 'Roy. Soc. Proc.,' A, vol. 111, p. 91 (1926).

Lines of O III in Gaseous Nebulæ.

A possibility of evaluating the $2p\,{}^3\mathrm{P}$ terms with greater accuracy is opened up by Bowen's recent important suggestion* that the two well-known green lines in the spectra of gaseous nebulæ may represent the irregular, or "forbidden," combinations $2p\,{}^3\mathrm{P}_2 - 2p\,{}^1\mathrm{D}_2$, $2p\,{}^3\mathrm{P}_1 - 2p\,{}^1\mathrm{D}_2$ of O III. This possibility is strengthened by the occurrence of a nebular line λ 4362·54, the wave-number of which (22912·5) corresponds closely with the irregular combination $2p\,{}^1\mathrm{D}_2 - 2p\,{}^1\mathrm{S}_0$. The somewhat similar assignment of other nebular lines to irregular combinations among the deeper terms of O II and N II increases the probability of Bowen's suggestion being correct. It is therefore desirable to examine the consequences of adopting the suggested O III origins of the three nebular lines in question.

If the interval 22913 indicated by λ 4362·54 be taken to represent the differences between Bowen's singlets noted above, it results that

	ν.	Δν.
$2p\,{}^1\mathrm{D}_2$	= 424385	
		22913
$2p\,{}^1\mathrm{S}_0$	= 401472	

The assignment of the green nebular lines to O III was based upon the fact that for these lines $\Delta\nu = 193$ is identical with $2p\,{}^3\mathrm{P}_1 - 2p\,{}^3\mathrm{P}_2$ of O III, and assuming this to be correct, the $2p\,{}^3\mathrm{P}$ terms at once follow. Thus :—

	λ	ν
Nebular line	5006·84	$19967 \cdot 1 = 2p\,{}^3\mathrm{P}_2 - 2p\,{}^1\mathrm{D}_2$,
,,	4958·91	$20160 \cdot 1 = 2p\,{}^3\mathrm{P}_1 - 2p\,{}^1\mathrm{D}_2$.

With $2p\,{}^1\mathrm{D}_2 = 424385$, already determined, and since $2p\,{}^3\mathrm{P}_0 - 2p\,{}^3\mathrm{P}_1 = 116$, it results that

$$2p\,{}^3\mathrm{P}_2 = 444352\,;\quad 2p\,{}^3\mathrm{P}_1 = 444545\,;\quad 2p\,{}^3\mathrm{P}_0 = 444661.$$

The value of $2p\,{}^3\mathrm{P}_2$ thus determined is as close as can be expected to that derived from the unresolved lines λ 374·3 and λ 305·7, and even if the nebular identifications are erroneous, it cannot be greatly in error. The values of the $2p\ {}^3P$ terms thus obtained with the aid of the nebular lines have accordingly been adopted in preference to those roughly indicated by unresolved multiplets in the extreme ultra-violet.

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* 'Nature,' vol. 120, p. 473 (Oct. 1, 1927); see also A. Fowler, 'Nature,' vol. 120, pp. 582 and 617 (October 22 and October 29).

If this be justified, it is of interest to note that the nebular lines may be utilised in this way for a calculation of the structures and positions, probably exact to about 0·001 A, of the unresolved multiplets λ 374·3 and λ 305·7, as shown below :—

	$2p\ {}^3P_2$ 444352	$2p\ {}^3P_1$ 444545	$2p\ {}^3P_0$ 444461
$3s\ {}^3P_0$ = 177336		267209 λ 374·239	
$3s\ {}^3P_1$ = 177218	267134 λ 374·344	267327 λ 374·074	267443 λ 373·911
$3s\ {}^3P_2$ = 176961	267391 λ 373·984	267584 λ 373·714	Observed λ = 374·3
$3d\ {}^3D_1$ = 117366	326986 λ 305·824	327179 λ 305·643	327295 λ 305·535
$3d\ {}^3D_2$ = 117317	327035 λ 305·778	327228 λ 305·597	
$3d\ {}^3D_3$ = 117243	327109 λ 305·708		Observed λ = 305·7

The terms which have been determined as above described are collected in Table II. The notation of Bowen, and that adopted for N II in the paper to which reference has been made, are indicated in order to facilitate comparisons. The quintet terms discovered by Mihul have not yet been found in combination with the triplets, and no attempt has been made to estimate their values.

Most of the triplet, and all of the quintet combinations have already been set out by Mihul, and it is not considered necessary to repeat them, except in so far as they are shown in the catalogue which follows.

The ionisation potential of O III as determined from the deepest ${}^3P$ term is 54·88 volts.

Table II.—Terms of O III.

Bowen.	N II.		*ν*.	*Δν*.
$a\,{}^3\mathrm{P}$	$1\,{}^3\mathrm{P}$	$2p\,{}^3\mathrm{P}_0$	444661	
				116
		${}^3\mathrm{P}_1$	444545	
				193
		${}^3\mathrm{P}_2$	444352	
$a\,{}^1\mathrm{D}$	$1\,{}^1\mathrm{D}_2'$	$2p\,{}^1\mathrm{D}_2$	424385	
$a\,{}^1\mathrm{S}$	$1\,{}^1\mathrm{S}_0'$	$2p\,{}^1\mathrm{S}_0$	401472	
$3k\,{}^3\mathrm{P}$	$1\,{}^3\mathrm{P}'$	$3s\,{}^3\mathrm{P}_0$	177336·21	
				118·36
		${}^3\mathrm{P}_1$	177217·85	
				256·94
		${}^3\mathrm{P}_2$	176960·91	
$3k\,{}^1\mathrm{P}$	$1\,{}^1\mathrm{P}_1'$	$3s\,{}^1\mathrm{P}_1$	171513·43	
$3m\,{}^1\mathrm{D}$	$2\,{}^1\mathrm{D}_2'$	$3p\,{}^1\mathrm{D}_2$	153636·88	
$3m\,{}^3\mathrm{D}$	$1\,{}^3\mathrm{D}'$	$3p\,{}^3\mathrm{D}_1$	150728·24	
				136·34
		${}^3\mathrm{D}_2$	150591·90	
				220·05
		${}^3\mathrm{D}_3$	150371·85	
$3m\,{}^3\mathrm{S}$	$1\,{}^3\mathrm{S}_1'$	$3p\,{}^3\mathrm{S}_1$	147036·00	
$3m\,{}^1\mathrm{S}_0$	$2\,{}^1\mathrm{S}_0'$	$3p\,{}^1\mathrm{S}_0$	146278·09	
$3m\,{}^3\mathrm{P}$	$2\,{}^3\mathrm{P}$	$3p\,{}^3\mathrm{P}_0$	144365·29	
				82·10
		${}^3\mathrm{P}_1$	144283·19	
				130·54
		${}^3\mathrm{P}_2$	144152·65	
$3m\,{}^1\mathrm{P}$	$1\,{}^1\mathrm{P}_1$	$3p\,{}^1\mathrm{P}_1$	130792·43	
	$1\,{}^1\mathrm{F}_3'$	$3d\,{}^1\mathrm{F}_3$	120132·09	
	$1\,{}^3\mathrm{F}'$	$3d\,{}^3\mathrm{F}_2$	120131·04	
				195·79
		${}^3\mathrm{F}_3$	119935·25	
				178·16
		${}^3\mathrm{F}_4$	119757·09	
$3n\,{}^1\mathrm{P}$	$1\,{}^1\mathrm{P}_1'''$	$3d\,{}^1\mathrm{P}_1$	119859·28	
$3n\,{}^3\mathrm{D}$	$1\,{}^3\mathrm{D}$	$3d\,{}^3\mathrm{D}_1$	117365·56	
				49·24
		${}^3\mathrm{D}_2$	117316·32	
				73·72
		${}^3\mathrm{D}_3$	117242·60	
$3n\,{}^3\mathrm{P}$	$1\,{}^3\mathrm{P}'''$	$3d\,{}^3\mathrm{P}_2$	115125·52	
				−114·00
		${}^3\mathrm{P}_1$	115011·52	
				−61·45
		${}^3\mathrm{P}_0$	114950·07	
$3n\,{}^1\mathrm{D}$	$1\,{}^1\mathrm{D}_2$	$3d\,{}^1\mathrm{D}_2$	111816·4	
$4k\,{}^3\mathrm{P}$	$2\,{}^3\mathrm{P}'$	$4s\,{}^3\mathrm{P}_0$	94484	
				115
		${}^3\mathrm{P}_1$	94599	
				258
		${}^3\mathrm{P}_2$	94857	
$4k\,{}^1\mathrm{P}$	$2\,{}^1\mathrm{P}_1'$	$4s\,{}^1\mathrm{P}_1$	91712 ?	
$4m\,{}^1\mathrm{D}$	$3\,{}^1\mathrm{D}_2'$	$4p\,{}^1\mathrm{D}_2$	78869·6	
$4m\,{}^3\mathrm{D}$	$2\,{}^3\mathrm{D}_1'$	$4p\,{}^3\mathrm{D}_1$	78106·59	
				107·10
		${}^3\mathrm{D}_2$	77999·49	
				207·03
		${}^3\mathrm{D}_3$	77792·46	
$4m\,{}^3\mathrm{S}$	$2\,{}^3\mathrm{S}_1'$	$4p\,{}^3\mathrm{S}_1$	76641·30	
$4m\,{}^1\mathrm{S}$	$3\,{}^1\mathrm{S}_0'$	$4p\,{}^1\mathrm{S}_0$	74993 ?	
$4m\,{}^3\mathrm{P}$	$3\,{}^3\mathrm{P}$	$4p\,{}^3\mathrm{P}_0$	74266·8	
				89·0
		${}^3\mathrm{P}_1$	74177·8	
				108·5
		${}^3\mathrm{P}_2$	74069·3	
$4m\,{}^1\mathrm{P}$	$2\,{}^1\mathrm{P}_1$	$4p\,{}^1\mathrm{P}_1$	72981 ?	
$b\ {}^5\mathrm{S}$	$\beta\,{}^5\mathrm{S}$	$2p'\,{}^5\mathrm{S}_2$	—	
$b\,{}^3\mathrm{D}$	$\beta\,{}^3\mathrm{D}$	$2p'\,{}^3\mathrm{D}_3$	324633	
				−28
		${}^3\mathrm{D}_{12}$	324605	
$b\,{}^3\mathrm{P}$	$\beta\,{}^3\mathrm{P}'$	$2p'\,{}^3\mathrm{P}_{12}$	302277	
				−16
		${}^3\mathrm{P}_0$	302261	
$b\,{}^1\mathrm{P}$	$\beta\,{}^1\mathrm{P}'$	$2p'\,{}^1\mathrm{P}_1$	234197	
$b\,{}^1\mathrm{D}$	$\beta\,{}^1\mathrm{D}$	$2p'\,{}^1\mathrm{D}_2$	—	
$b\,{}^3\mathrm{S}$	$\beta\,{}^3\mathrm{S}$	$2p'\,{}^3\mathrm{S}_1$	247572	

Catalogue of O III Lines.

The observations included in the present catalogue (Table III) extend from the red to λ 2228 in the ultra-violet. Other observations, extending to about λ 820 are still under discussion in connection with the probable presence of lines representing higher stages of ionisation than O III. It is possible, indeed, that some of the unclassified lines in the present list may be of this character, as the experimental evidence for the distinction is not very conclusive.

The wave-lengths (in I.A.) and intensities are given in the first column, the wave-numbers (*in vacuo*) in the second, and the classification in the third. Lines enclosed in brackets have been calculated from multiplet structures. The position of the faint lines on the red side of λ 3962 have been determined only with small dispersion and should be regarded as approximate. Bowen's classified lines in the extreme ultra-violet, with three additions, and Mihul's quintet identifications have been included in the catalogue for the sake of completeness.

It should be noted that there is evidence of instability of the wave-lengths of certain groups of lines, especially in the $^3D\ ^3F$ multiplets, and that consequently some of the tabulated wave-lengths are subject to revision by as much as 0·1 A. This question of variable wave-lengths in oxygen and certain other elements is under separate investigation.

Table III.—Catalogue and Classification of O III Lines.

λ.	ν	Classification.
5592·37 (6)	17876·55	$3s\,{}^1P_1-3p\,{}^1D_2$
5508·11 (1)	18150·0	
5268·06 (2)	18977·0	$3p\,{}^1P_1-3d\,{}^1D_2$
4569·50 (1*n*)	21878·1	
4555·30 (0)	21946·3	
4538·8 (0*n*)	22026·1	
4534·0 (0*n*)	22049·4	
4529·7 (00)	22070·3	
4482·78 (1*n*)	22301·3	
4474·95 (1*n*)	22340·4	
4470·9 (00*n*)	22360·6	
4461·56 (1)	22407·4	
4458·44 (1*n*)	22423·1	
4454·00 (1*n*)	22445·5	
4440·1 (0)	22515·7	
4435·4 (00*n*)	22539·6	
4434·43 (2*n*)	22544·5	
4430·2 (00*n*)	22566·0	
4424·3 (00*n*)	22596·1	
4408·14 (1*n*)	22679·0	
4389·3 (00*n*)	22776·3	
4385·73 (0)	22794·8	
*4379·55 (3*n*)	22827·0	
*4376·15 (1*n*)	22844·7	
4239·5 (00)	23581·1	$3s\,{}^3P_1-3p\,{}^1D_2$
4177·8 (00)	23929·3	
4125·5 (00*n*)	24232·7	
4081·10 (1)	24496·3	
4073·90 (0)	24539·6	
3971·2 (00)	25774·2	
3961·59 (8)	25235·34	$3d\,{}^1P_1-3p\,{}^1S_0$
3951·82 (0)	25297·66	
3935·0 (2*n*)	25405·8	
3869·1 (1*nn*)	25838·5	
3816·75 (1)	26192·60	
3810·96 (2)	26232·69	$3s\,{}^3P_2-3p\,{}^3D_1$
3791·26 (6)	26369·00	$3s\,{}^3P_2-3p\,{}^3D_2$
3774·00 (6)	26489·59	$3s\,{}^3P_1-3p\,{}^3D_1$
3759·87 (9)	26589·06	$3s\,{}^3P_2-3p\,{}^3D_3$
3757·21 (5)	26607·96	$3s\,{}^3P_0-3p\,{}^3D_1$
3754·67 (7)	26625·96	$3s\,{}^3P_1-3p\,{}^3D_2$
3734·80 (1)	26767·61	${}^5D_2-{}^5P_3$
3733·20 (0)	26779·08	
3732·13 (1)	26786·76	$3p\,{}^3P_2-3d\,{}^3D_1$

* Erroneously entered in list of O II lines (' Roy. Soc. Proc.,' A, vol. 110, p. 481).

Table III—(continued).

λ.	ν.	Classification.	λ.	ν.	Classification.
3729·70 (1)	26804·21		3362·38 (4)	29732·33	${}^5P_3-{}^5P_2'$
3728·70 (1)	26811·40		3355·92 (3)	29789·56	
3725·30 (3)	26835·87	$3p\ {}^3P_2-3d\ {}^3D_2$	3350·99 (4)	29833·38	${}^5P_3-{}^5P_3'$
3721·95 (1)	26860·02	${}^5D_1-{}^5P_2$	3350·68 (3)	29836·14	${}^5P_2-{}^5P_1'$
3720·86 (3)	26867·89	${}^5D_3-{}^5P_3$	3348·05 (2)	29859·58	
3719·82 (00)	26875·40		3344·26 (2)	29893·42	${}^5P_2-{}^5P_2'$
3715·08 (6)	26909·69	$3p\ {}^3P_2-3d\ {}^3D_3$	3340·74 (6)	29924·91	$3s\ {}^3P_2-3p\ {}^3S_1$
3714·50 (0)	26913·90		3336·78 (3)	29960·42	${}^5P_1-{}^5P_1'$
3714·03 (2)	26917·30	$3p\ {}^3P_1-3d\ {}^3D_1$	3333·00 (4)	29994·40	${}^5P_2-{}^5P_3'$
3712·48 (2)	26928·54	${}^5D_2-{}^5P_2$	3332·49 (1)	29999·17	
3709·52 (2)	26950·13	${}^5D_0-{}^5P_1$	3330·40 (4)	30017·82	${}^5P_1-{}^5P_2'$
3707·24 (6)	26966·60	$3p\ {}^3P_1-3d\ {}^3D_2$	3326·16 (0)	30056·08	
3704·73 (3)	26984·88	${}^5D_1-{}^5P_1$	3312·30 (5)	30181·85	$3s\ {}^3P_1-3p\ {}^3S_1$
3703·37 (5)	26994·77	${}^5D_4-{}^5P_3$	3305·77 (0)	30241·33	$3p\ {}^3D_3-3d\ {}^3F_2$
3702·75 (5)	26999·30	$3p\ {}^3P_0-3d\ {}^3D_1$	3299·36 (3)	30300·21	$3s\ {}^3P_0-3p\ {}^3S_1$
3698·70 (5)	27028·86	${}^5D_3-{}^5P_2$	3284·57 (4)	30436·65	$3p\ {}^3D_3-3d\ {}^3F_3$
3695·37 (4)	27053·22	${}^5D_2-{}^5P_1$	3281·94 (3)	30461·04	$3p\ {}^3D_2-3d\ {}^3F_2$
3653·00 (1)	27367·0		3269·04 (0)	30581·23	
3650·70 (0)	27384·2		3267·31 (5)	30597·43	$3p\ {}^3D_1-3d{}^3F_2$
3649·20 (00)	27395·5		3265·46 (10)	30614·76	$3p\ {}^3D_3-3d\ {}^3F_4$
3647·70 (0)	27406·8		3260·98 (8)	30656·82	$3p\ {}^3D_2-3d\ {}^3F_3$
3646·84 (2)	27413·2		3258·77 (0)	30677·61	
3645·20 (1)	27425·6		3257·20 (1)	30692·39	
3638·70 (3)	27474·5		3254·50 (0)	30717·86	
3556·92 (1)	28106·2		3252·94 (2)	30732·63	$3p\ {}^3D_2-3d\ {}^1P_1$
3531·39 (0)	28309·4		3238·57 (5)	30868·95	$3p\ {}^3D_1-3d\ {}^1P_1$
[3475·26]	[28766·6]	${}^5D_4-{}^5F_3$	3207·67 (1)	31166·30	
3466·90 (0)	28835·98	${}^5D_3-{}^5F_2$	3200·95 (1)	31231·73	
3466·15 (2)	28842·22	${}^5D_4-{}^5F_4$	3132·86 (6)	31910·50	$3p\ {}^3S_1-3d\ {}^3P_2$
3464·20 (1*n*)	28858·5		3121·71 (5)	32024·47	$3p\ {}^3S_1-3d\ {}^3P_1$
3459·98 (2)	28893·66	${}^5D_3-{}^5F_3$	3115·73 (4)	32085·93	$3p\ {}^3S_1-3d\ {}^3P_0$
3459·52 (0)	28897·50	${}^5D_2-{}^5F_1$	3088·04 (2)	32373·64	
3455·12 (5)	28934·12	${}^5D_4-{}^5F_5$	3084·76 (1)	32408·05	
3454·90 (2)	28936·14	${}^5D_2-{}^5F_2$	3059·30 (6)	32677·74	$3s\ {}^3P_2-3p\ {}^3P_1$
3451·33 (1)	28966·07	${}^5D_1-{}^5F_1$	3047·13 (8)	32808·25	$3s\ {}^3P_2-3p\ {}^3P_2$
3450·94 (4)	28969·34	${}^5D_3-{}^5F_4$	3043·02 (5)	32852·56	$3s\ {}^3P_1-3p\ {}^3P_0$
†[3448·02]	[28993·7]	${}^5D_2-{}^5F_3$	3035·43 (4)	32934·70	$3s\ {}^3P_1-3p\ {}^3P_1$
3447·22 (1)	29000·60	${}^5D_0-{}^5F_1$	3034·32 (0)	32946·75	$3d\ {}^1D_2-4p\ {}^1D_2$
3446·73 (2)	29004·73	${}^5D_1-{}^5F_2$	3024·57 (4)	33052·96	$3s\ {}^3P_0-3p\ {}^3P_1$
3444·10 (5)	29026·87	$3p\ {}^3P_2-3d\ {}^3P_2$	3024·36 (1)	33055·25	$3p\ {}^3D_2-3d\ {}^3D_3$
3440·39 (4)	29058·17		3023·45 (5)	33065·20	$3s\ {}^3P_1-3p\ {}^3P_2$
3435·42 (1)	29100·21		3017·63 (5)	33128·97	$3p\ {}^3D_3-3d\ {}^3D_3$
3430·60 (4)	29141·09	$3p\ {}^3P_2-3d\ {}^3P_1$	3008·79 (3)	33226·30	$3p\ {}^3D_1-3d\ {}^3D_2$
3428·67 (3)	29157·50	$3p\ {}^3P_1-3d\ {}^3P_2$	3004·35 (4)	33275·40	$3p\ {}^3D_2-3d\ {}^3D_2$
3427·41 (3*n*)	29168·22		2997·71 (2)	33349·10	$3p\ {}^3D_3-3d\ {}^3D_2$
3423·42 (1*n*)	29202·21		2996·51 (3)	33362·46	$3p\ {}^3D_1-3d\ {}^3D_1$
3415·29 (3)	29271·72	$3p\ {}^3P_1-3d\ {}^3P_1$	2992·11 (2)	33411·51	$3p\ {}^3D_2-3d\ {}^3D_1$
3411·74 (1)	29302·18		2983·78 (9)	33504·79	$3p\ {}^1D_2-3d\ {}^1F_3$
3408·13 (1)	29333·22	$3p\ {}^3P_1-3d\ {}^3P_0$	2983·66 (1)	33506·13	$3p\ {}^1D_2-3d\ {}^3F_2$
3405·74 (2)	29353·80	$3p\ {}^3P_0-3d\ {}^3P_1$	2959·68 (5)	33777·60	$3p\ {}^1D_1-3d\ {}^1P_1$
3403·58 (1)	29372·43		2836·34 (4)	35246·36	$3p\ {}^3D_3-3d\ {}^3P_2$
3394·26 (1)	29453·08		2818·68 (1)	35467·18	$3p\ {}^3D_2-3d\ {}^3P_2$
3384·95 (4)	29534·09		2809·63 (3)	35581·42	$3p\ {}^3D_2-3d\ {}^3P_1$
3383·85 (2)	29543·69		2798·91 (1)	35717·69	$3p\ {}^3D_1-3d\ {}^3P_1$
3382·69 (3)	29553·82		2794·09 (2)	35779·30	$3p\ {}^3D_1-3d\ {}^3P_0$
3381·27 (0)	29566·23		2756·22 (1)	36270·9	$3p\ {}^1D_2-3d\ {}^3D_1$
3369·40 (00)	29670·38	$3p\ {}^3S_1-3d\ {}^3D_1$	2752·47 (0)	36320·3	$3p\ {}^1D_2-3d\ {}^3D_2$
3363·83 (1)	29719·51	$3p\ {}^3S_1-3d\ {}^3D_2$	2739·15 (0)	36496·9	

† Masked by O II.

Table III—(continued).

λ.	ν.	Classification.	λ.	ν.	Classification.
2735·14 (1)	36550·4		2529·36 (1)	39523·8	$3p\,^3D_3-4p\,^3D_3$
2726·95 (1)	36660·2		2517·36 (1)	39712·2	
2713·40 (2)	26843·2	$3d\,^3P_0-4p\,^3D_1$	2516·11 (00)	39730·5	
2710·37 (0)	36884·4		2512·41 (0)	39790·4	
2708·87 (1)	36904·8	$3d\,^3P_1-4p\,^3D_1$	2507·73 (1)	39864·7	
2701·05 (3)	37011·7	$3d\,^3P_1-4p\,^3D_2$	*2504·7 (00*n*)	39913	
2696·00 (3)	37081·0		2501·78 (00)	39959·5	
2695·49 (6)	37088·0		2499·22 (00)	40000·4	
2692·74 (1)	37125·9	$3d\,^3P_2-4p\,^3D_2$	2493·74 (1)	40083·3	
2691·54 (00)	37142·4		2493·37 (1)	40094·3	
2688·04 (00)	37190·8		2492·2 (00*n*)	40113	
2687·53 (5)	37197·9		2489·0 (00)	40165	
2686·14 (10)	37217·1	$^5P_3-{}^5S_2$	2488·3 (00*n*)	40176	
2684·88 (1*n*)	37234·6		2485·27 (00)	40224·9	
2683·65 (4)	37251·6		2483·24 (0)	40257·8	
2681·42 (2*n*)	37282·6		2482·60 (0)	40268·2	
2677·81 (3*n*)	37332·9	$3d\,^3P_2-4p\,^3D_3$	2480·73 (1)	40298·7	
2677·08 (1)	37343·0		2475·73 (00)	40379·9	
2674·57 (8)	37378·1	$^5P_2-{}^5S_2$	2474·57 (0)	40398·8	
2669·97 (2*n*)	37442·5		2458·1 (00)	40670	
2665·69 (7)	37502·6	$^5P_1-{}^5S_2$	2457·8 (00)	40674	$3d\,^3D_2-4p\,^3S_1$
2661·57 (0)	37560·7				
*2628·31 (1*n*)	38036				
2625·7 (0*n*)	38074		2454·99 (8)	40721·0	$3s\,^1P_1-3p\,^1P_1$
2624·69 (0)	38088·39				
*2623·0 (1*n*)	38113				
2622·32 (2)	38122·8		2454·21 (0)	40734·0	
2620·10 (0)	38155·1		2453·54 (2*n*)	40745·1	$3d\,^3P_1-4p\,^3P_0$
2618·82 (00)	38173·8		2451·91 (2*n*)	40772·2	$3d\,^3P_0-4p\,^3P_1$
2617·00 (1)	38200·3		2451·09 (0*n*)	40785·8	
*2616·2 (00*n*)	38212		2450·06 (2*n*)	40803·0	
2609·59 (4)	38308·76	$3d\,^3P_0-4p\,^3S_1$	2449·38 (2*n*)	40814·3	
2605·41 (6)	38370·22	$3d\,^3P_1-4p\,^3S_1$	2448·21 (1*n*)	40833·8	$3d\,^3P_1-4p\,^3P_1$
2597·69 (8)	38484·23	$3d\,^3P_2-4p\,^3S_1$	2446·92 (00)	40855·3	
2596·79 (00)	38497·6		2441·72 (2*n*)	40942·3	$3d\,^3P_1-4p\,^3P_2$
2593·72 (0)	38543·1		2441·41 (00)	40947·5	$3d\,^3P_2-4p\,^3P_1$
2588·23 (0)	38624·9		2441·06 (2*n*)	40953·4	
2582·92 (1*n*)	38701·3		2438·83 (5*u*)	40990·8	$3d\,^1P_1-4p\,^1D_2$
2580·70 (00)	38737·6		2438·05 (00)	41004·0	
2578·27 (00)	38774·1		2434·96 (2*n*)	41056·0	$3d\,^3P_2-4p\,^3P_2$
2577·17 (0)	38790·6		2431·69 (0*n*)	41112·2	
2576·11 (1)	38806·6		2429·65 (0*n*)	41145·7	
*2572·5 (0*n*)	38861		2429·35 (1*n*)	41150·8	
*2569·6 (0*n*)	38905		2426·94 (2*n*)	41191·6	
2569·11 (1)	38912·3		2426·35 (0*n*)	41201·7	
2566·53 (00)	38951·5		2425·93 (2*n*)	41208·8	
2558·06 (8)	39080·41	$3p\,^1P_1-4s\,^1P_1$?	2422·84 (5*n*)	41261·3	$3d\,^1F_2-4p\,^1D_2$
2555·64 (0)	39117·4		2421·2 (00*n*)	41289	
2549·62 (2)	39209·8	$3p\,^3D_2-4p\,^3D_1$	2401·51 (0*n*)	41627·8	
2547·45 (2)	39243·2	$3p\,^3D_3-4p\,^3D_2$	2399·25 (0*n*)	41667·0	
2546·43 (4)	39258·9	$3p\,^3D_1-4p\,^3D_1$	2398·97 (00*n*)	41671·8	
2542·68 (5)	39316·8	$3p\,^3D_2-4p\,^3D_2$	2394·33 (5*n*)	41752·6	$3d\,^1P_1-4p\,^3D_1$
2541·80 (00*n*)	39330·4		2390·44 (8*n*)	41820·5	$3p\,^1D_2-3d\,^1D_2$
2540·1 (00)	39357		2388·20 (1)	41859·8	$3d\,^1P_1-4p\,^3D_2$
2539·50 (2)	39366·0	$3p\,^3D_1-4p\,^3D_2$	2383·92 (6*n*)	41934·9	$3d\,^3F_3-4p\,^3D_2$
2534·08 (6*n*)	39450·2	$3p\,^3D_3-4p\,^3D_3$	2382·32 (7*n*)	41963·1	$3d\,^3F_4-4p\,^3D_3$
2532·5 (00)	39475		2378·90 (4*n*)	42023·4	$3d\,^3F_2-4p\,^3D_1$
2531·8 (00)	39486		2372·82 (2*n*)	42131·1	$3d\,^3F_2-4p\,^3D_2$

* Very diffuse.

Table III—(continued).

λ.	ν.	Classification.
2372·21 (3n)	42142·0	$3d\,{}^3F_3-4p\,{}^3D_3$
2345·02 (0n)	42630·5	
2327·97 (1n)	42942·7	
2324·83 (0n)	43000·7	O II ?
2319·52 (2n)	43099·1	$3p\,{}^3D_1-4p\,{}^3P_0$
2317·37 (3n)	43139·1	$3p\,{}^3D_2-4p\,{}^3P_1$
2315·52 (4n)	43173·6	$3p\,{}^3D_3-4p\,{}^3P_2$
2314·76 (2n)	43187·7	$3p\,{}^3D_1-4p\,{}^3P_1$
2311·58 (2)	43247·1	$3p\,{}^3D_2-4p\,{}^3P_2$
2308·70 (1n)	43301·1	O III ?
2306·04 (00)	43351·0	
2295·51 (00)	43549·9	
2288·36 (00)	43685·9	
2288·12 (00)	43690·5	
2287·21 (1n)	43707·9	
2285·66 (2n)	43737·5	
2285·07 (00n)	43749	
2252·84 (0n)	44374·6	
2228·15 (3n)	44866·3	$3d\,{}^1P_1-4p\,{}^1S_0$
2132·50 (1)	46878·5	$3d\,{}^1P_1-4p\,{}^1P_1$?
λ vac.		
1916·48 (2)	52179	$3p\,{}^3S_1-4s\,{}^3P_2$
1907·06 (1)	52437	$3p\,{}^3S_1-4s\,{}^3P_1$
1902·89 (1)	52552	$3p\,{}^3S_1-4s\,{}^3P_0$
	Observations by Bowen.	
835·288 (9)	119719·2	$2p\,{}^3P_2-2p'\,{}^3D_3$
835·094 (3)	119747·0	$2p\,{}^3P_2-2p'\,{}^3D_{12}$
833·741 (8)	119941·3	$2p\,{}^3P_1-2p'\,{}^3D_{12}$
832·926 (7)	120058·7	$2p\,{}^3P_0-2p'\,{}^3D_1$
703·853 (7)	142075·1	$2p\,{}^3P_2-2p'\,{}^3P_{12}$
702·898 (6)	142268·2	$2p\,{}^3P_1-2p'\,{}^3P_{12}$
702·817 (6)	142284·5	$2p\,{}^3P_1-2p'\,{}^3P_0$
702·327 (6)	142383·8	$2p\,{}^3P_0-2p'\,{}^3P_1$
*658·4 (0)	151883	$2p'\,{}^3P_2-3p\,{}^3D_3$
*644·159 (6)	155241	$2p'\,{}^3P_{12}-3p\,{}^3S_1$. Also O II.
597·82 (4)	167274	$2p\,{}^1S_0-2p'\,{}^1P_1$
525·79 (6)	190190	$2p\,{}^1D_2-2p'\,{}^1P_1$
508·180 (6)	196781	$2p\,{}^3P_2-2p'\,{}^3S_1$
507·684 (5)	196973	$2p\,{}^3P_1-2p'\,{}^3S_1$
507·384 (4)	197089	$2p\,{}^3P_0-2p'\,{}^3S_1$
434·91 (2)	229933	$2p\,{}^1S_0-3s\,{}^1P_1$
395·52 (2)	252832	$2p\,{}^1D_2-3s\,{}^1P_1$
374·3 (4)	267165	$2p\,{}^3P-3s\,{}^3P$
335·06 (0)	281643	$2p\,{}^1S_0-3d\,{}^1P_1$
328·34 (0)	304562	$2p\,{}^1D_2-3d\,{}^1P_1$
305·7 (3)	327118	$2p\,{}^3P-3d\,{}^3D$
*303·7 (2)	329272	$2p\,{}^3P-3d\,{}^3P$

* Suggested by present author.

Comparison of O III with N II.

It is of interest to compare the terms of O III with those of N II, as in Table IV, where the relations between the two are shown in the form of the ratios O III : N II.

As regards the triplets, there is no ambiguity in the assignment of term types, and for these it will be seen that the ratios increase continuously from 1·862 in the $2p$ level to a maximum slightly in excess of 2·25 (= 9R/4R) in the $3d$ level. The variations are similar to those found in corresponding comparisons of other spectra. For example, in comparing the doublet terms of Al III with those of Mg II,* it may be deduced that the ratios for the deepest s, p and d levels are 1·89, 2·05 and 2·28 respectively.

In consequence of the absence of extended sequences, it is difficult to assign the types of singlet terms in complex spectra with the same certainty as for triplets. In the case of O III, however, there can be little doubt as to the correct assignment of the $p\,{}^1D_2$ terms, or of $3d\,{}^1P_1$, and thence of $3d\,{}^1D_2$. The

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* A. Fowler, 'Roy. Soc. Proc.,' A, vol. 103, p. 427 (1923).

Table IV.—Comparison of Terms of O III and N II.

N II.	O III.	N II.	O III.	O III/N II.
$1\,{}^3P_0$	$2p\,{}^3P_0$	238849	444661	1·862
$1\,{}^1D_2'$	$2p\,{}^1D_2$	223531	424385	1·899
$1\,{}^1S_0'$	$2p\,{}^1S_0$	147119	401472	2·729
$1\,{}^3P_0'$	$3s\,{}^3P_0$	89937	177336	1·972
$1\,{}^1P_1'$	$3s\,{}^1P_1$	89658	171513	1·913
$2\,{}^1D_2'$	$3p\,{}^1D_2$	74235	153637	2·069
$1\,{}^3D_1'$	$3p\,{}^3D_1$	72324	150728	2·084
$1\,{}^3S_1'$	$3p\,{}^3S_1$	69954	147036	2·102
$2\,{}^1S_0'$	$3p\,{}^1S_0$	60573	146278	2·415
$2\,{}^3P_0$	$3p\,{}^3P_0$	68273	144365	2·115
$1\,{}^1P_1$	$3p\,{}^1P_1$	64634	130792	2·023
$1\,{}^1F_3'$	$3d\,{}^1F_3$	52168	120132	2·302
$1\,{}^3F_2'$	$3d\,{}^3F_2$	52334	120131	2·296
$1\,{}^1P_1'''$	$3d\,{}^1P_1$	51755	119859	2·316
$1\,{}^3D_1$	$3d\,{}^3D_1$	51408	117365	2·285
$1\,{}^3P_0'''$	$3d\,{}^3P_2$	49909†	115126†	2·307
$1\,{}^1D_2$	$3d\,{}^1D_2$	48726	111816	2·294
$2\,{}^3P_0'$	$4s\,{}^3P_0$	42306	94484	2·234
$2\,{}^1P_1'$	$4s\,{}^1P_1$	40987	91712 ?	2·238
$3\,{}^1D_2'$	$4p\,{}^1D_2$	*37045 ?	78869	2·129
$2\,{}^3D_1'$	$4p\,{}^3D_1$	36132	78107	2·162
$2\,{}^3S_1'$	$4p\,{}^3S_1$	35314	76641	2·170
$3\,{}^1S_0'$	$4p\,{}^1S_0$		74993 ?	
$3\,{}^3P_0$	$4p\,{}^3P_0$	*33035	74267	2·249
$3\,{}^1P_1$	$4p\,{}^1P_1$		72981 ?	

* Added to N II in the course of the present investigation.
† Inverted terms.

$3p\,{}^1S_0$ and $3p\,{}^1P_1$ terms might possibly be considered as interchangeable, but the apparent occurrence of $3p\,{}^1P_1 - 3d\,{}^1D_2$ (18977) is substantial support for the assignments adopted. The magnitudes of these terms are also in favour of the arrangement shown in the table, since $3p\,{}^1S_0$ (146278) unites with $2p\,{}^1S_0$ (401472) in a formula with a small correcting term, whereas the substitution of $3p\,{}^1P_1$ (130792) for $3p\,{}^1S_0$ would require a large correcting term.

There is greater difficulty with regard to the singlets of N II, and the comparision with O III suggests some modification of the original allocations. Thus, consideration of magnitudes suggests that $1\,{}^1D_2$ and $1\,{}^1P'''$ of N II should be interchanged, and since this is in no way inconsistent with the observed combinations, these terms have been interchanged in Table IV. With this modification, the ratios for the singlets are in reasonable agreement with those for triplets, except for $2p\,{}^1S_0$ and $3p\,{}^1S_0$, which are notably discordant. An interchange of $3p\,{}^1S_0$ (60573) and $3p\,{}^1P_1$ (64634) would not entirely remove the discordance, and would lead to an irregular combination $^1S_0 - ^1D_2$ for the line 15908·28 (3). These terms have accordingly been left in their original form. The terms $2p\,^1S_0$ and $3p\,^1S_0$ of N II thus remain much smaller than would be expected from the comparison with O III, but they involve strong lines and no alternative term values have yet been found.

Summary.

The paper includes a catalogue of more than 300 lines attributed to O III, of which about one-half have been classified by the author and others. As was expected, the spectrum is generally similar to that of N II, and the terms so far determined are in complete agreement with Hund's theory.

The assigned term values are based upon a sequence of three singlet D terms. The deepest term is of the type $^3P_0$, and for this the value 444661 has been determined by adopting Bowen's suggestion that the well-known green lines λ 5006·8, λ 4958·9 in the spectra of gaseous nebulæ are due to irregular combinations of deep terms of O III. The corresponding ionisation potential of O III is 54·88 volts.

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The Arc Spectrum of Carbon.

By A. Fowler, D.Sc., F.R.S., Yarrow Research Professor of the Royal Society, and E. W. H. Selwyn, B.Sc., Imperial College, South Kensington.

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Introductory.

It is well known that in the region of observation extending from the red to λ 2000 the spectrum of an ordinary carbon arc shows only a single line, λ 2478. Merton and Johnson, however, have observed a considerable number of lines which they have attributed to the neutral atom of carbon in the spectrum of a vacuum tube containing a trace of an oxide of carbon in helium at 20 to 30 mm. pressure.* Another method of developing the lines of C I, in this case almost perfectly free from lines of C II, has recently been described by J. W. Ryde.† In these experiments, a carbon arc was fed with currents up to 250 amperes, the potential drop across the arc being 60 to 80 volts. Many of the lines assigned to C I by Merton and Johnson then appeared with great intensity, together with lines of N I, O I, and A I from the atmospheric gases, the lines in question being localised in a region near the negative pole of the arc.

With additional observations made during the present investigation, the spectrum of neutral carbon is now sufficiently well known to justify an attempt to extend the analysis of the spectrum, which has already been partially elucidated by Bowen‡ from lines observed in the extreme ultra-violet.

Experimental.

Photographs of the spectrum of an oxide of carbon in helium, as in Merton and Johnson's experiments, have been taken with the vacuum grating spectrograph, covering the region λ 1250 to λ 2760 in the first order and λ 1250 to λ 1380 in the second order. Some of the lines have also been photographed in higher orders with other sources. The effect of admixture with helium is to emphasise the known lines of C I with respect to those of C II which appear in company with them, and to introduce additional lines, of which many are probably due to C I. The lines which remain after eliminating bands of carbon* and lines of oxygen, mercury, nitrogen, and ionised carbon, and omitting those which appear in the list of classified lines (Table VI), are shown in Table I.

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* 'Roy. Soc. Proc.,' A, vol. 103, p. 384 (1923); vol. 108, p. 343 (1925).

† 'Roy. Soc. Proc.,' A, vol. 117, p. 164 (1927).

‡ 'Phys. Rev.,' vol. 29, p. 238 (1927).

Table I.—Unclassified Lines in Helium-Carbon.

Merton and Johnson.	λ.	ν.	λ.	ν.	λ.	ν.
	2665·24 (0*n*)	37509	2385·85 (1)	41901	1361·27 (1)	73461
	2664·48 (0*n*)	37520	2268·50 (2)	44068	1359·42 (1)	73561
	2663·04 (1)	37540	2042·24 (2)	48950	1357·21 (1)	73681
2661·7 (0)	2661·90 (1)	37556	2005·0 (0)	49859	1331·83 (1)	75085
2660·3 (1)	2660·33 (1)	37578	λ vac.		1321·77 (1)	75656
	2658·50 (0)	37604	1993·65 (2)	50159	1313·50 (1)	76132
	2639·42 (0)	37876	1765·4 (0)	56644	1311·36 (2)	76257
	2602·90 (0)	38407	1764·0 (0)	56689	1283·11 (1)	77936
	2592·30 (0*n*)	38564	1481·75 (5)	67487	1280·75 (2)	78079
2582·9 (2)	2582·85 (1)	38705	1472·3 (0)	67920	1280·33 (3)	78105
2567·7 (0)	2567·78 (0)	38932	1470·20 (1)	68018	1279·85 (1)	78134
2515·15 (1)		39747	1468·5 (0)	68097	1279·17 (2)	78176
2439·6 (0)		40978	1467·48 (3)	68144		
2413·9 (0)		41414	1364·20 (2)	73303		

Several of the brighter lines of C I in Merton and Johnson's list were noted as rather feeble lines in the spectra of ordinary carbon dioxide vacuum tubes photographed some years ago. It has since been found that these lines can be obtained quite prominently, and comparable in intensity with many of the lines of C II, by merely raising the pressure of the gas to about 20 mm. All but the very faint lines of Merton and Johnson's list in the region λ 4740–λ 6600 have been observed by this method. The C I spectrum under these conditions would seem to resemble that obtained by Ryde's high-current arc more closely than that given by the helium-carbon vacuum tube, as, for example, in the absence of the lines λλ 4758·78 and 4757·59.

Results similar to those of Ryde, but excluding some of the fainter lines, have been obtained with currents much smaller than those employed by him. Thus, it was found that while the lines in question could not be seen at all with the ordinary currents of 5 to 10 amperes on a 110-volt circuit, they appeared with considerable intensity in the neighbourhood of the negative pole when the current was increased to 15 or 20 amperes. The lines so obtained are in excellent agreement with those tabulated by Ryde. By the use of the valuable neocyanine plates of the Eastman-Kodak Company, this method has been utilised to extend the observations as far as λ 10120 in the near infra-red, and the lines which have been observed, other than those listed by Ryde, are shown in Table II. As the dispersion employed was about 100 A. per millimetre, no great accuracy can be claimed for the tabulated wave-lengths.

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* Some of these carbon bands could only be distinguished from lines by comparison with other plates in which the band spectrum was more strongly developed (*cf.* Jevons, 'Phil. Mag.,' vol. 47, p. 586 (1924)).

Table II.—Infra-Red Lines of Carbon Arc.

λ.	ν.	Remarks.
10119 (0)	9880	Possibly C I. See Table V.
9661 (0)	10348	$\Delta\nu$ suggests C I. See Table IV.
9623 (0)	10389	
9407 (2)	10627	Probably C I. See Table V.
9394 (0)	10642	
9264·7 (0)	10790·7	O I (Paschen).
9190·6	10877·7	$\Delta\nu$ suggests N I.
9170·2	10901·9	
9142·1	10935·4	
9111·4	10972·2	C I multiplet. See Table IV.
9094·5	10992·7	
9088·5	10999·9	
9078·1	11012·5	
9061·8	11032·3	
*8336·4	11992·3	Carbon line.

* Occurs in Ryde's list of lines of unknown origin. Other lines of nitrogen and oxygen fall between λ 9061 and λ 8336.

The conspicuous multiplet beginning with λ 9111 and the singlet λ 8336 have been proved to be due to carbon by their observation in the spectrum of carbon dioxide and their absence from the spectrum of oxygen. The origins of other lines are somewhat uncertain, as the vacuum-tube observations were not successful beyond λ 9111. It is possible, however, that the pair of lines λλ 9661, 9623 and the lines λλ 10119, 9407 are due to C I, as they yield values of the order expected for terms of this spectrum.

The poles used in the experiments on the arc spectrum were rods of Acheson graphite, and were practically free from impurities. It was found convenient to use thin or sharply pointed carbon poles in order to localise the stream in which the C I lines appeared.

In connection with the foregoing observations, it is important to note that the spectrum of the ordinary carbon arc, with small current, in so far as it is represented by an arc in an atmosphere of nitrogen, has been found to show the principal lines of C I in the region more refrangible than λ 2000, including the strong line at λ 1931. These lines also occur, together with lines of C II, in the spectra of the carbon vacuum arc, vacuum tubes containing carbon compounds, and the "hot spark" of carbon investigated by Millikan and Bowen.

It thus appears that all the ordinary sources yield lines of C I which arise from combinations of the deeper terms of the spectrum, and that special methods only become necessary for the excitation of lines due to combinations of terms representing higher energy levels. The observations of the arc recall those of A. S. King,* who similarly found that in metallic arcs with currents of about 1000 amperes there was an increased development of lines of the neutral atom due to higher terms, while lines due to ionised atoms were not notably modified.

Predicted Terms.

The terms of C I predicted by the Heisenberg-Hund theory are similar to those for N II† and O III‡ and are shown in Table III. The notation is on the system adopted for O III, terms in each row being prefixed by the n_k designation of the corresponding orbit of the series electron. Under ordinary circumstances, combinations between terms on different rows are regulated by the familiar rules, applicable in this notation to the *electron* symbols, and by the rule for inner quantum numbers as applied to the *term* symbols. Dashes are applicable to the electron symbols alone, and only become necessary when there is more than one family of terms. In the case of C I the need for distinguishing terms of similar type on the same row does not arise. Other singlet, triplet and quintet terms appear when one of the three 2_2 electrons represented in the last row of the table is removed to successively higher orbits.

Table III.—Predicted Terms of C I.

K	L		M			N			Electrons in unclosed groups.	Terms.						
1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3								
2	2	2							$s^2 p^2$	$2p$	$^3\mathrm{P}$	$^1\mathrm{D}_2$	$^1\mathrm{S}_0$			
2	2	1	1						$s^2 p . s$	$3s$	$^3\mathrm{P}$	$^1\mathrm{P}_1$				
2	2	1		1					$s^2 p . p$	$3p$	$^3\mathrm{D}$	$^3\mathrm{P}$	$^3\mathrm{S}$	$^1\mathrm{D}_2$	$^1\mathrm{P}_1$	$^1\mathrm{S}_0$
2	2	1			1				$s^2 p . d$	$3d$	$^3\mathrm{F}$	$^3\mathrm{D}$	$^3\mathrm{P}$	$^1\mathrm{F}_3$	$^1\mathrm{D}_2$	$^1\mathrm{P}_1$
2	2	1				1			$s^2 p . s$	$4s$	$^3\mathrm{P}$	$^1\mathrm{P}$				
2	2	1					1		$s^2 p . p$	$4p$	$^3\mathrm{D}$	$^3\mathrm{P}$	$^3\mathrm{S}$	$^1\mathrm{D}_2$	$^1\mathrm{P}_1$	$^1\mathrm{S}_0$
2	2	1						1	$s^2 p . d$	$4d$	$^3\mathrm{F}$	$^3\mathrm{D}$	$^3\mathrm{P}$	$^1\mathrm{F}$	$^1\mathrm{D}$	$^1\mathrm{P}$
2	1	3							$s p^3$	$2p'$	$^5\mathrm{S}$	$^3\mathrm{D}$	$^3\mathrm{P}$	$^3\mathrm{S}$	$^1\mathrm{D}_2$	$^1\mathrm{P}_1$

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* 'Astrophys. J.,' vol. 62, p. 238 (1925).

† A. Fowler and L. J. Freeman, 'Roy. Soc. Proc.,' A, vol. 114, p. 672 (1927).

‡ A. Fowler, 'Roy. Soc. Proc.,' A, vol. 117, p. 317 (1928).

Combinations involving some of the deeper terms have already been identified by Bowen, namely, $2p\,^3P - 2p'\,^3P$, $2p\,^3P - 2p'\,^3D$, $2p\,^3P - 3s\,^3P$. In addition, he has suggested that a partially resolved line at λ 1277 represents $2p\,^3P - 3d\,^3D$, and, by assuming that $3d\,^3D$ has one-quarter of its value for N II, finds a probable value of 91300 for $2p\,^3P$. Bowen has found confirmation of the two pp' combinations in the fact that they follow the irregular doublet law when compared with corresponding combinations of N II, O III and F IV. Comparison with O III and N II (Table VII) also shows that the magnitudes of the p' terms are inappropriate for the main family of terms.

Triplet Combinations.

The four triplet combinations identified by Bowen, with one addition, are shown in the first part of Table IV. The $2p\,^3P - 3d\,^3D$ multiplet has been resolved into two components, and the table indicates a provisional attempt to show the structure of this group, the separation $^3D_1 - {}^3D_2$ being merely estimated. A similar attempt has been made to represent the structure of the other multiplets.

The second part of Table IV shows the probable combinations with the second deepest triplet term, $3s\,^3P$. These include all the $3p$ and $4p$ triplet terms except $3p\,^3D$, which probably gives a group of lines in the infra-red just beyond the limit of the present photographs. Two lines observed in this region at λ 9661 and λ 9623, approximately, have been taken to represent the first two lines of the triplet $3s\,^3P - 3p\,^3S$; they have only been photographed in the high-current arc in air, and there is no independent evidence of their carbon origin. The resulting value of $3p\,^3S$, however, is of the magnitude expected.

It is of interest to note that the $3d\,^3P$ term is inverted, exactly as the corresponding terms of O III and N II. It may also be remarked that Merton and Johnson's lines, λλ 4758 and 4757, which were not found by Ryde, do not form part of the multiplet $3s\,^3P - 4p\,^3P$.

Three $p\,^3P$ terms are available for the calculation of triplet term values. The computed formula for these is

$$p\,^3P_0 = R/[m + 0{\cdot}719265 - 0{\cdot}616474/m]^2 \quad R = 109737\,;\ m = 1, 2, 3,$$

giving $2p\,^3P_0 = 90230$, $3p\,^3P_0 = 18878$, $4p\,^3P_0 = 8888$. The correcting term, however, is so large that the formula cannot be relied upon to give closely approximate values. The formula for the sequence of three singlet $p\,^1D$ terms, on the other hand, involves a very small correcting term, and the calculated values are much more likely to be near the true values. A similar result was

Table IV.—Triplet Combinations.

	$2p\,^3P_2$ 90975·0	*27·5*	$2p\,^3P_1$ 91002·5	*14·8*	$2p\,^3P_0$ 91017·3
$3s\,^3P_0$ = 30686·0			60316·5 (2)		
20·0			*20·1*		
$3s\,^3P_1$ = 30666·0	60308·9 (2)	*27·7*	60336·6 (2)	*13·1*	*60349·7 (3)
40·1	*40·8*		*40·0*		
$3s\,^3P_2$ = 30625·9	*60349·7 (3)	*26·9*	60376·6 (2)		
$2p'\,^3D_3$ = 26929·1	64045·9 (5)				
−2·1					
$2p'\,^3D_2$ = 26927·0	[64048·0]		64075·5 (4)		
−1·3					
$2p'\,^3D_1$ = 26925·7	[64049·3]		[64076·8]		64091·6 (3)
$2p'\,^3P_{210}$ = 15763·5	75211·6 (4)	*27·3*	75238·9 (4)	*14·8*	75253·7 (3)
$3d\,^3D_1$ = [12714·5]	[78260]		[78288]		[78303]
[5·0]					
$3d\,^3D_2$ = 12709·5	[78265]		78293 (1)		
9·5					
$3d\,^3D_3$ = 12700·0	78275 (2)				
$3d\,^3P_2$ = 11709	79266 (2)		[79293]		
−10					
$3d\,^3P_1$ = 11699	[79276]		79303 (1)	*15*	79318 (0)
[−5]					
$3d\,^3P_0$ = [11694]			[79308]		
	$3s\,^3P_2$ 30625·9	*40·0*	$3s\,^3P_1$ 30666·0	*20·0*	$3s\,^3P_0$ 30686·0
$3p\,^3D$	Out of range.				
$3p\,^3S_1$ = 20278 ?	10348	*41*	10389		
$3p\,^3P_0$ = 19666·1			10999·9 (1)		
12·5			*12·6*		
$3p\,^3P_1$ = 19653·6	10972·2 (1)	*40·3*	11012·5 (1)	*19·8*	*11032·3 (4)
20·4	*20·5*		*19·8*		
$3p\,^3P_2$ = 19633·2	10992·7 (4)	*40·1*	*11032·3 (4)		
$4p\,^3D_1$ = 10833·5	[19792·5]		[19832·5]		19852·5 (0)
7·0					
$4p\,^3D_2$ = 10826·5	[19799·5]		19839·5 (3)		
29·8					
$4p\,^3D_3$ = 10796·7	19829·2 (3)				
$4p\,^3S_1$ = 9913·7	20712·2 (1)	*40·4*	20752·6 (1)	*19·4*	†20772·0 (1)
$4p\,^3P_0$ = 9707·5			20958·5 (2)		
14·5			*14·8*		
$4p\,^3P_1$ = 9693·0	20932·7 (3)	*40·6*	20973·3 (2)	*18·6*	*20991·9 (4)
18·0	*18·2*		*18·6*		
$4p\,^3P_2$ = 9675·0	20950·9 (4)	*41·0*	*20991·9 (4)		

* Used twice. † Occurs in Ryde's list of unknown lines.

found for the corresponding terms of O III, and the calculated singlet terms have accordingly been adopted. Since no intercombinations of singlets and triplets have yet been recognised, the triplet terms have been adjusted so as to give triplet and singlet terms in the same order as in O III and N II. From the comparative list of term values in Table VII, it will be seen that the $3d$ terms of each type show only small variations in the three spectra, and the value 12700 assigned to $3d\,^3D_3$ (or 12714·5 to $3d\,^3D_1$) cannot be greatly in error. It is to be understood, however, that the triplet and singlet terms have not yet been brought into exact relation with each other.

Numbers enclosed in square brackets represent calculated wave-numbers of lines forming parts of multiplets, or term values which have merely been estimated.

Singlets.

The classification of singlets in C I presents considerable difficulties, because there are no extended series and many of the expected lines must occur either in the near infra-red or in the Schumann region. Some of the lines, however, can be classified with considerable certainty from a general consideration of the predicted terms in relation to the already known terms of N II and O III. Thus, there can be no doubt that the strong lines λ 2478 and λ 1931* represent $2p\,^1S_0 - 3s\,^1P_1$ and $2p\,^1D_2 - 3s\,^1P_1$ respectively, since these combinations should give the strongest of all the singlets. The three brightest lines in the visible spectrum, λλ 5380, 5052, 4932, can also be classified with almost equal certainty. Again, the interval between the lines λ 1751 and λ 1459 appears to be the same as that between $2p\,^1D_2$ and $2p\,^1S_0$ and would seem to justify the identification of the common combining term as $3d\,^1P_1$.

The terms $2p\,^1D_2$ and $4p\,^1D_2$ having been determined from some of these lines, an approximate value for $3p\,^1D_2$ could be derived by interpolation. This suggested the line λ 9407 ($\nu = 10627$) as $3p\,^1D_2 - 3d\,^1P_1$, and assuming this to be correct, a sequence of three $p\,^1D_2$ terms became available for a more precise determination of singlet term values, to replace those which had been provisionally adopted. The calculated formula is

$$p\,^1D_2 = R/[m + 0{\cdot}168835 - 0{\cdot}007117/m]^2 \qquad R = 109737\,;\ m = 1, 2, 3.$$

This gives $2p\,^1D_2 = 81311{\cdot}5$, and other singlet terms have been determined, with this as a basis, from the combinations shown in Table V. The more doubtful term identifications are distingushed by a ? mark.

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* Millikan and Bowen have assigned λ 1931 to C III ('Phys. Rev.,' vol. 26, p. 316 (1925)), but this is altogether in contradiction with the experimental evidence, since this line occurs in the ordinary arc in air, where neither C II nor C III lines are present. There is another line, however, at λ 1923 which appears under strong discharges, and is doubtless the C III line anticipated by Millikan and Bowen.

Table V.—Singlets of C I.

		$2p\,^1D_2$ 81312	*11452*	$2p\,^1S_0$ 69860	$3s\,^1P_1$ 29526	$3p\,^1D_2$ 23406 ?	$3p\,^1S_0$?	$3p\,^1P_1$ 19646 ?
$3s\,^1P_1$	= 29526	51786 (10)	*11452*	40334 (10)	——	* *	* *	‡9880 ?
$3d\,^1F_3$	= 12979?	68333 (5)		——	——		——	——
$3d\,^1P_1$	= 12779	68533 (3)	*11452*	57081 (5)	——	†10627 (3)	* *	* *
$3d\,^1D_2$	= 11414?			——	——	§11992 (3)	——	
$4s\,^1P_1$								
$4p\,^1D_2$	= 10945	——		——	18581 (8)	——	——	——
$4p\,^1S_0$	= 9738	——		——	19788 (6)	——	——	——
$4p\,^1P_1$	= 9256	——		——	20270 (5)	——	——	——
$4d\,^1F_5$				——	——		——	——
$4d\,^1P_1$	= 7475?	73837 (1)		62379 (3)	——			
$4d\,^1D_2$				——	——		——	

† Used for calculation of $3p\,^1D_2$.
‡ Used for calculation of $3p\,^1P_1$.
§ Used for calculation of $3d\,^1D_2$.
* * Out of range.
—— Not expected.

As will appear from the blank spaces where lines might be expected, further progress in the identification of terms must depend largely upon the possibility of extending the observations farther into the infra-red, and of obtaining more complete development of the C I lines in the Schumann region.

List of Classified Lines.

The lines which have been classified, in some cases merely tentatively, are included in Table VI. In view of the disturbances of wave-lengths in the high-current arc, Merton and Johnson's vacuum-tube wave-lengths have been adopted in preference to those of Ryde for the region λ 5380 to λ 2478. The wave-lengths for which no authorities are quoted in the footnotes have been determined in the course of the present investigation.

Table VI.—Classified Lines of C I.

λ air.	ν.	Classification.
10119	9880	$3s\,{}^1\mathrm{P}_1-3p\,{}^1\mathrm{P}_1$?
9661	10348	$3s\,{}^3\mathrm{P}_2-3p\,{}^3\mathrm{S}_1$?
9623	10389	$3s\,{}^3\mathrm{P}_1-3p\,{}^3\mathrm{S}_1$?
9407	10627	$3p\,{}^1\mathrm{D}_2-3d\,{}^1\mathrm{P}_1$
9111·4 (2)	10972·2	$3s\,{}^3\mathrm{P}_2-3p\,{}^3\mathrm{P}_1$
9094·5 (5)	10992·7	$3s\,{}^3\mathrm{P}_2-3p\,{}^3\mathrm{P}_2$
9088·5 (1)	10999·9	$3s\,{}^3\mathrm{P}_1-3p\,{}^3\mathrm{P}_0$
9078·1 (1)	11012·5	$3s\,{}^3\mathrm{P}_1-3p\,{}^3\mathrm{P}_1$
9061·8 (4)	11032·3	$3s\,{}^3\mathrm{P}_1-3p\,{}^3\mathrm{P}_2$ $3s\,{}^3\mathrm{P}_0-3p\,{}^3\mathrm{P}_1$
8336·4 (5)	11992·3	$3p\,{}^1\mathrm{D}_2-3d\,{}^1\mathrm{D}_2$?
*5380·242 (8)	18581·37	$3s\,{}^1\mathrm{P}_1-4p\,{}^1\mathrm{D}_2$
*5052·122 (6)	19788·16	$3s\,{}^1\mathrm{P}_1-4p\,{}^1\mathrm{S}_0$
*5041·66 (3)	19829·2	$3s\,{}^3\mathrm{P}_2-4p\,{}^3\mathrm{D}_3$
*5039·05 (3)	19839·5	$3s\,{}^3\mathrm{P}_1-4p\,{}^3\mathrm{D}_2$
*5035·75 (0)	19852·5	$3s\,{}^3\mathrm{P}_0-4p\,{}^3\mathrm{D}_1$
*4932·00 (5)	20270·1	$3s\,{}^1\mathrm{P}_1-4p\,{}^1\mathrm{P}_0$
*4826·73 (1)	20712·2	$3s\,{}^3\mathrm{P}_2-4p\,{}^3\mathrm{S}_1$
*4817·33 (1)	20752·6	$3s\,{}^3\mathrm{P}_1-4p\,{}^3\mathrm{S}_1$
†4812·84 (1)	20772·0	$3s\,{}^3\mathrm{P}_0-4p\,{}^3\mathrm{S}_1$
*4775·87 (3)	20932·7	$3s\,{}^3\mathrm{P}_2-4p\,{}^3\mathrm{P}_1$
*4771·72 (4)	20950·9	$3s\,{}^3\mathrm{P}_2-4p\,{}^3\mathrm{P}_2$
*4770·00 (2)	20958·5	$3s\,{}^3\mathrm{P}_1-4p\,{}^3\mathrm{P}_0$
*4766·62 (2)	20973·3	$3s\,{}^3\mathrm{P}_1-4p\,{}^3\mathrm{P}_1$
*4762·41 (4)	20991·9	$3s\,{}^3\mathrm{P}_1-4p\,{}^3\mathrm{P}_2$ $3s\,{}^3\mathrm{P}_0-4p\,{}^3\mathrm{P}_1$
*2478·525 (10)	40334·39	$2p\,{}^1\mathrm{S}_0-3s\,{}^1\mathrm{P}_1$

λ vac.	ν.	Classification.
‡1931·027 (10)	51785·9	$2p\,{}^1\mathrm{D}_2-3s\,{}^1\mathrm{P}_1$
1751·90 (5)	57080·9	$2p\,{}^1\mathrm{S}_0-3d\,{}^1\mathrm{P}_1$
§1658·13 (2)	60308·9	$2p\,{}^3\mathrm{P}_2-3s\,{}^3\mathrm{P}_1$
§1657·92 (2)	60316·5	$3p\,{}^3\mathrm{P}_1-3s\,{}^3\mathrm{P}_0$
§1657·37 (2)	60336·6	$2p\,{}^3\mathrm{P}_1-3s\,{}^3\mathrm{P}_1$
§1657·01 (3)	60349·7	$2p\,{}^3\mathrm{P}_2-3s\,{}^3\mathrm{P}_2$ $2p\,{}^3\mathrm{P}_0-3s\,{}^3\mathrm{P}_1$
§1656·27 (2)	60376·6	$2p\,{}^3\mathrm{P}_1-3s\,{}^3\mathrm{P}_2$
1603·10 (3)	62379·1	$2p\,{}^1\mathrm{S}_0-4d\,{}^1$
§1561·381 (5)	64045·9	$2p\,{}^3\mathrm{P}_2-2p'\,{}^3\mathrm{D}_3$
§1560·660 (4)	64075·5	$2p\,{}^3\mathrm{P}_1-2p'\,{}^3\mathrm{D}_2$
§1560·267 (3)	64091·6	$2p\,{}^3\mathrm{P}_0-2p'\,{}^3\mathrm{D}_1$
1463·43 (5)	68332·6	$2p\,{}^1\mathrm{D}_2-3d\,{}^1$
1459·15 (3)	68533·0	$2p\,{}^1\mathrm{D}_2-3d\,{}^1$
1354·34 (1)	73836·7	$2p\,{}^1\mathrm{D}_2-4d\,{}^1$
§1329·583 (4)	75211·6	$2p\,{}^3\mathrm{P}_2-2p'\,{}^3\mathrm{P}$
§1329·100 (4)	75238·9	$2p\,{}^3\mathrm{P}_1-2p'\,{}^3\mathrm{P}$
§1328·839 (3)	75253·7	$2p\,{}^3\mathrm{P}_0-2p'\,{}^3\mathrm{P}$
1277·54 (3)	78275	$2p\,{}^3\mathrm{P}_2-3d\,{}^3$
1277·26 (2)	78293	$2p\,{}^3\mathrm{P}_1-3d\,{}^3$
1261·57 (2)	79266	$2p\,{}^3\mathrm{P}_2-3d\,{}^3\mathrm{P}_2$
1260·99 (1)	79303	$2p\,{}^3\mathrm{P}_1-3d\,{}^3\mathrm{P}_1$
1260·75 (0)	79318	$2p\,{}^3\mathrm{P}_0-3d\,{}^3\mathrm{P}_1$

* λ Merton and Johnson.
† λ Ryde, not in Merton and Johnson's list.
‡ λ Bowen and Ingram (' Phys. Rev.,' vol. 28, p. 445 (1926)).
§ λ Bowen (' Phys. Rev.,' vol. 29, p. 238 (1927)).

Comparison with N II *and* O III.

A close similarity between the spectra of C I, N II and O III is to be expected from the general theory, since the three atoms are similarly constituted. Each has six external electrons, but the nuclear charge is 6 for C I, 7 for N II and 8 for O III. A general comparison of the terms of the three spectra is given in Table VII, those of O III having been divided by 9 and those of N II by 4. The triplet separations of O III and N II have been similarly reduced for easier comparison with those of C I.

Table VII.—Terms of O III, N II and C I.

	O III/9.	$\Delta\nu/9$.	N II/4.	$\Delta\nu/4$.	C I.	$\Delta\nu$.
$2p\,^3P_0$	49406·8		59712·25		91017·3	
		12·7		12·55		14·8
$^3P_1$	49393·9		59699·7		91002·5	
		21·8		21·0		27·5
$^3P_2$	49372·1		59678·7		90975·0	
$2p\,^1D_2$	47153·9		55882·7		81312	
$2p\,^1S_0$	44608·0		*[36779·7]		69860	
$3s\,^3P_0$	19704·0		22484·3		30686·0	
		13·1		7·9		20·0
$^3P_1$	19690·9		22476·4		30666·0	
		28·6		34·1		40·1
$^3P_2$	19662·3		22442·3		30625·9	
$3s\,^1P_1$	19057·0		22414·5		29526	
$3p\,^1D_2$	17070·8		18558·8		23406	
$3p\,^3D_1$	16747·6		18081·0		Out of range.	
		15·2		15·4		
$^3D_2$	16732·4		18065·6			
		24·4		23·8		
$^3D_3$	16708·0		18041·8			
$3p\,^3S_1$	16337·3		17489		20746 ?	
$3p\,^1S_0$	16253·1		*[15143·1]			
$3p\,^3P_0$	16040·6		17068·3		19666·1	
		9·1		8·8		12·5
$^3P_1$	16031·5		17059·5		19653·6	
		14·5		14·6		20·4
$^3P_2$	16017·0		17044·9		19633·2	
$3p\,^1P_1$	13421·4 ?		16158·4			
$3d\,^1F_3$	13348·0		13042·0		12979 ?	
$3d\,^3F_2$	13347·9		13083·6			
		21·8		14·9		
$^3F_3$	13326·1		13068·7			
		19·8		20·4		
$^3F_4$	13306·3		13048·3			
$3d\,^1P_1$	13317·7		12938·6		12779	
$3d\,^3D_1$	13040·6		12852·1		†[12715]	
		5·5		6·0		[5·0]
$^3D_2$	13035·1		12846·1		12710	
		8·1		7·6		10·0
$^3D_3$	13027·0		12838·5		12700	

* Identifications somewhat doubtful.
† Estimated by probable $\Delta\nu$.

Table VII—(continued).

	O III/9.	$\Delta\nu$/9.	N II/4.	$\Delta\nu$/4.	C I.	$\Delta\nu$.
$3d\ ^3P_2$	12791·7	−12·6	12497·2	−13·0	11709	−10·0
$^3P_1$	12779·1	−6·9	12484·2	−7·0	11699	[−5·0]
$^3P_0$	12772·2		12477·2		*[11694]	
$3d\ ^1D_2$	12424·0		12181·4		11414 ?	
$4s\ ^3P_2$	†		10576·4	12·9		
$^3P_1$			10563·5	29·9		
$^3P_0$			10533·6			
$4s\ ^1P_1$	10190·2 ?		10246·9			
$4p\ ^1D_2$	8763·3		9261 ?		10945	
$4p\ ^3D_1$	8678·5	11·9	9032·9	12·7	10833·5	7·0
$^3D_2$	8666·6	23·0	9020·2	24·0	10826·5	29·3
$^3D_3$	8643·6		8996·2		10796·7	
$4p\ ^3S_1$	8515·7		8828·5		9913·7	
$4p\ ^1S_0$	8332·5 ?				9738	
$4p\ ^3P_0$	8251·9	9·9	8258·9	7·7	9707·5	14·5
$^3P_1$	8242·0	12·1	8251·2	12·0	9693·0	18·0
$^3P_2$	8229·9		8239·2		9675·0	
$4p\ ^1P_1$	8109 ?				9256	
$2p'\ ^3D_3$	36070		36652		26731	
$2p'\ ^3P_{12}$	33586		32408		15565	
$2p'\ ^1P_1$						
$2p'\ ^1D_2$						
$2p'\ ^3S_1$	20930		27508			

* Estimated by probable $\Delta\nu$.
† Previous identification in O III considered doubtful.

A perfect correlation of the terms is scarcely possible, because for each spectrum the values have been obtained by the use of a formula which is only approximate. The term values for O III and C I have been determined from a sequence of three singlet $p\,^1D$ terms in each case, and those for N II from a sequence of three $s\,^3P$ terms. A recomputation for N II, using a third $p\,^1D$ term which has since been identified, merely increases all the term values by about 18 units, which may be considered negligible. In all these formulæ, however, the correcting terms to the Rydberg formula are very small, so that the tabulated values for the three spectra are unlikely to be much in error relatively to each other.

A regular progression in most of the term values in passing from O III to C I is clearly shown in the table. In particular it will be observed that the $3d$ terms vary very slightly in the three spectra and that this fact justifies the adoption of 12700 as an approximate value for $3d\,^3D_3$ in C I, on which the values of the remaining triplet terms of this spectrum have been based. This value clearly cannot be much in error, but since intercombinations of triplets and singlets have not been identified in C I, the triplet and singlet term values are not necessarily correct with respect to each other in this spectrum. The adoption of this value, however, results in giving the terms of C I in the same order of magnitude as those of the other two spectra.

The $p\,^1S_0$ terms of N II, as already noted in a previous comparison with O III,* are very discordant. Interpolation of $2p\,^1S_0$ between O III and C I, with the aid of the "irregular doublet" law, suggests a value of about 206000 (= 51500 when divided by 4), but no support for this can be found in the observations of N II. This term should combine strongly with $3s\,^1P_1$, and produce a line near λ 862, but no line has been observed in this position. At the same time, the $3s\,^1P_1$ term may be considered to be well established, because it combines with $2p\,^1D_2$, as deduced from the nebular spectrum, to give a line at λ 746·9, and the adopted value of $2p\,^1D_2$ is itself supported by an observed combination with $3d\,^1D_2$, as determined from the laboratory spectrum. Thus, adopting Bowen's suggestion that the separation of two red nebular lines is identical with $2p\,^3P_1 - 2p\,^3P_2$ of N II, and identifying these lines as $2p\,^3P_{21} - 2p\,^1D_2$ we have

From laboratory observations.	Nebular lines.		Supposed combinations.
	λ	ν	
$2p\,^3P_0 = 238849$			
$2p\,^3P_1 = 238799$	6548·1	15267·4	$2p\,^3P_1 - 2p\,^1D_2$
$2p\,^3P_2 = 238715$	6585·6	15184·8	$2p\,^3P_2 - 2p\,^1D_2$

therefore $2p\,^1D_2 = 223531$.

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* 'Roy. Soc. Proc.,' A, vol. 117, p. 317 (1928).

The value of $2p\,^1D_2$ thus determined is strongly supported by the following combinations :—

$$\begin{array}{rl} 2p\,^1D_2 &= 223531 \\ \text{(Lab.) } 3s\,^1P_1 &= 89658 \\ \hline \text{Calc. line} &= 133873 \\ &= \lambda\, 746\cdot 98 \\ \text{Obs. line} &= \lambda\, 746\cdot 97 \end{array} \qquad \begin{array}{rl} 2p\,^1D_2 &= 223531 \\ \text{(Lab.) } 3d\,^1D_2 &= 51754 \\ \hline \text{Calc. line} &= 171777 \\ &= \lambda\, 582\cdot 15 \\ \text{Obs. line} &= \lambda\, 582\cdot 16 \end{array}$$

Thus, there can be little doubt that the $3s\,^1P_1$ term of N II has been correctly determined, and, for the present, the $2p\,^1S_0$ and $3p\,^1S_0$ terms of this spectrum must be regarded as anomalous. The corresponding terms of O III and C I, however, appear to be normal.

Another way of comparing the terms of the three spectra, which is more useful in some respects, is by the application of the " irregular doublet " law, which has been so successfully utilised by Millikan and Bowen for the identification of lines observed by them in the extreme ultra-violet. For similarly constituted atoms this law takes the form, for spectroscopic terms,

$$\sqrt{T/R} = \frac{1}{n}\,(Z - s),$$

where T represents a term, R the Rydberg constant, n the principal quantum number, Z the atomic number, and s the screening constant, which is not very different for corresponding terms of the three spectra. It follows that $\sqrt{T/R}$ and Z should show an approximately linear relationship for terms of the same type which have the same principal quantum number. The linear law accordingly provides a valuable test of the identifications of the three sets of terms.

In the first place it will be instructive to compare the triplet terms, for the reason that these have been identified with greater certainty than the singlets, and the nature of the regularity to be expected in the singlets will be more clearly indicated.

Table VIII shows the values of $\sqrt{T/R}$ for the three sets of terms and the differences between them. The near equality of the differences on the same row may be taken as an indication that the terms have been correctly identified. The three C I terms which have not yet been identified yield lines in the infra-red, but approximate values for them may be found by interpolation if desired. The screening constants may be derived from the tabulated values of $\sqrt{T/R}$ by multiplying these values by the appropriate principal quantum numbers and subtracting the results from the atomic numbers. Thus, for the $2p\,^3P_0$

Table VIII.—Values of $\sqrt{T/R}$ for Triplet Terms.

	O III.	Difference.	N II.	Difference.	C I.
$2p\ ^3P_0$	2·013	*0·538*	1·475	*0·564*	0·911
$3s\ ^3P_0$	1·272	*0·366*	0·906	*0·377*	0·529
$3p\ ^3D_1$	1·172	*0·360*	0·812		
$3p\ ^3S_1$	1·157	*0·359*	0·798	*0·363*	0·435 ?
$3p\ ^3P_0$	1·147	*0·358*	0·789	*0·366*	0·423
$3d\ ^3F_2$	1·046	*0·356*	0·690		
$3d\ ^3D_1$	1·034	*0·350*	0·684	*0·344*	0·340
$3d\ ^3P_0$	1·024	*0·349*	0·675	*0·348*	0·327
$4s\ ^3P_0$	0·928	*0·307*	0·621		
$4p\ ^3D_1$	0·844	*0·270*	0·574	*0·260*	0·314
$4p\ ^3S_1$	0·836	*0·269*	0·567	*0·266*	0·301
$4p\ ^3P_0$	0·823	*0·274*	0·549*	*0·251*	0·298

* Identified since paper on N II was published.

terms the screening constants are 3·97 (O III), 4·05 (N II) and 4·18 (C I). The reduction in screening with increase of atomic number is presumably accounted for by the greater relative distance of the orbit from the core of the atom.

The values of $\sqrt{T/R}$ for the singlet terms are shown in Table IX.

Table IX.—Values of $\sqrt{T/R}$ for Singlet Terms.

	O III.	Difference.	N II.	Difference.	C I.
$2p\ ^1D_2$	1·966	*0·539*	1·427	*0·566*	0·861
$2p\ ^1S_0$	1·913				0·798
$3s\ ^1P_1$	1·250	*0·346*	0·904	*0·385*	0·519
$3p\ ^1D_2$	1·183	*0·361*	0·822	*0·360*	0·462
$3p\ ^1S_0$	1·157				
$3p\ ^1P_1$	1·049 ?	*0·282 ?*	0·767	*0·344*	0·423 ?
$3d\ ^1F_3$	1·046	*0·356*	0·690	*0·346*	0·344
$3d\ ^1P_1$	1·045	*0·358*	0·687	*0·346*	0·341
$3d\ ^1D_2$	1·009	*0·343*	0·666	*0·344*	0·322 ?
$4s\ ^1P_1$	0·914	*0·303*	0·611		
$4p\ ^1D_2$	0·848	*0·267*	*0·581	*0·265*	0·316
$4p\ ^1S_0$	0·827				
$4p\ ^1P_1$	0·816 ?	*0·272 ?*	0·544	*0·253*	0·291

* Identified since paper on N II was published.

Apart from the $p\ ^1S_0$ terms, which have already been considered, most of the identifications of the singlet terms appear to be justified by the progressive values of the differences shown in the table. The $3p\ ^1P_1$ and $4p\ ^1P_1$ terms were already considered doubtful in O III, and the above comparison suggests that the provisional identification of $3p\ ^1P_1$, at least, is improbable.

The above equation for $\sqrt{T/R}$ may be extended to combinations between terms with principal quantum numbers n_1 and n_2, as follows :—

$$\frac{T_1}{R} - \frac{T_2}{R} = \frac{\nu}{R} = \frac{(Z - s_1)^2}{n_1^2} - \frac{(Z - s_2)^2}{n_2^2}$$
$$= [(n_2^2 - n_1^2)\,Z^2 - 2\,(n_2^2 s_1 - n_1^2 s_2)\,Z + n_2^2 s_1^2 - n_1^2 s_2^2]/n_1^2 n_2^2,$$

which shows that an approximately linear relationship is to be expected between Z and the wave-numbers of lines, when both terms involved have the same principal quantum numbers. This is illustrated in Table X.

Table X.—Linear Relations between Corresponding Lines.

Line.	C I.	Difference.	N II.	Difference.	O III.	Difference.	F IV.
$3s\,^3P_2 - 3p\,^3P_2$	10993	*10597*	21590	*11218*	32808		
$3p\,^1D_2 - 3d\,^1P_1$	10627	*11854*	22481	*11297*	33778		
$2p\,^3P_2 - 2p'\,^3D_3$	64048	*28072*	92120	*27627*	119747	*27487*	147234
$2p\,^3P_2 - 2p'\,^3P_2$	75212	*33875*	19087	*32988*	142075	*32552*	174627

Millikan and Bowen have shown* that although a linear relationship should not exist for lines whose terms have different principal quantum numbers, such a relation is to be expected for numbers obtained by reducing the wave-numbers of these lines by the formula

$$\nu' = \nu - (Z - A)^2\,(n_2^2 - n_1^2)/n_1^2 n_2^2,$$

where A is a number whose value is chosen convenient for calculation. Assigning a value of 5 to A, this procedure has been adopted for corresponding lines of the three spectra, as shown in Table XI.

It will be seen that the approximate linear relations shown in Tables X and XI justify the classification of the lines in question, with the possible exception of $2p\,^1D_2 - 3s\,^1P_1$. The identifications of these lines in the three spectra, however, appear to be well founded.

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* 'Phys. Rev.,' vol. 26, p. 314 (1925).

Table XI.—Further Linear Relations between Corresponding Lines.

Line.		ν.	ν'.	Difference.
$2p\,^1D_2-3s\,^1P_1$	C I	51786	36545	36364
	N II	133873	72909	42758
	O III	252832	115667	
$2p\,^3P_2-3s\,^3P_2$	C I	60350	45109	42880
	N II	148943	87989	42011
	O III	267165	130000	
$2p\,^1D_2-3d\,^1P_1$	C I	68533	53292	57521
	N II	171778	110813	57584
	O III	304562	167397	
$2p\,^3P_2-3d\,^3D_3$	C I	78275	63034	63433
	N II	187431	126467	63486
	O III	327118	189953	
$2p\,^3P_2-3d\,^3P_2$	C I	79266	64025	63727
	N II	*[188716]	127752	64355
	O III	329272	192107	

* Calculated line.

Triplet Separations.

As regards the separations of the triplet terms indicated in Table VII, it will be observed that $\Delta\nu/9$ for O III and $\Delta\nu/4$ for N II are nearly equal for most of the corresponding terms. In N II the $3s\,^3P$ separations are somewhat anomalous, but the sum of the two separations is practically identical with the corresponding sum in O III. The $3d\,^3F$ separations in the two spectra are also slightly discordant.

The most notable feature of the separations in C I is that they are generally greater than the reduced separations in the other two spectra.

Sommerfeld's "regular doublet" law, which Millikan and Bowen have found to be applicable to many optical spectra of similarly constituted atoms, does not appear to hold for the spectra under consideration, with the exception of the $2p\,^3P$ terms. This law takes the form

$$\Delta\nu = \frac{R\alpha^2 (Z - s)^4}{n^3 k (k - 1)},$$

where R is the Rydberg constant, α the relativity constant ($\alpha^2 = 5 \cdot 31 \times 10^{-5}$), Z the atomic number, s a screening constant, n the principal quantum number, and k has its usual values, 2 for P, 3 for D terms, and so on. $R\alpha^2 = 5 \cdot 83$, and it is thus found that $R\alpha^2/n^3\, k\, (k - 1)$ is 0·365 for 2P, 0·108 for 3P and 0·0456 for 4P. Some of the results for the spectra in question are as follows :—

	$2p\,^3P_0 - 2p\,^3P_2$.			$3p\,^3P_0 - 3p\,^3P_2$.			$4p\,^3P_0 - 4p\,^3P_2$.		
	$\Delta\nu$	$\sqrt[4]{\Delta\nu/0 \cdot 365}$	s	$\Delta\nu$	$\sqrt[4]{\Delta\nu/0 \cdot 108}$	s	$\Delta\nu$	$\sqrt[4]{\Delta\nu/0 \cdot 0456}$	s
C I	42	3·275	2·725	33	4·181	1·819	33	5·166	0·834
N II	134	4·377	2·623	94	5·433	1·567	78	6·431	0·569
O III	309	5·394	2·606	213	6·665	1·335	197	8·108	−0·108
F IV	637*	6·464	2·536						

* I. S. Bowen, 'Phys. Rev.,' vol. 29, p. 242 (1927).

It will be observed that while the calculated values of s are consistent in each case, they show a diminution, in place of the expected increase, towards a maximum of 5, in passing from $2p\,^3P$ to $4p\,^3P$.

Landé's modified formula† also leads to unexpected results. This may be written in the form

$$\Delta\nu = \frac{R\alpha^2 C^2 (Z - s)^2}{(n^*)^3 \,.\, k (k - 1)},$$

where n^* is the Rydberg denominator $[C^2R/(n^*)^2 = \nu]$, $C = 1$ for neutral atoms, 2 for singly ionised atoms, and so on, and s is a screening constant. The formula may also be written

$$\Delta n^* = \frac{\alpha^2}{2k (k - 1)} \,.\, (Z - s)^2.$$

The application of this formula gives the following results for some of the terms in question :—

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† 'Z. f. Physik,' vol. 25, p. 49 (1924).

	$2p\,^3P_0-2p\,^3P_2$.				$3p\,^3P_0-3p\,^3P_2$.		
	$\Delta\nu$	$\Delta n^*\times 10^6$	$Z-s$	s	$\Delta\nu$	$\Delta n^*\times 10^6$	$Z-s$
C I	42	253	4·366	1·634	33	1979	12·21
N II	134	381	5·357	1·643	94	1738	11·44
O III	309	524	6·283	1·717	213	1925	12·04

The results for $2p\,^3P$ are in close agreement, but for $3s\,^3P$, $3p\,^3P$ and $4p\,^3P$ the calculated values of $Z - s$ are greater than Z itself, and the formula is clearly not applicable to the determination of s from these spectra.

Summary.

Further observations of the arc spectrum of carbon (C I) have been made, and the classification of the lines has been considerably extended. The deepest term is a triplet P_0, the value of which is estimated at 91017, corresponding to an ionisation potential of 11·2 volts. Comparisons are made with the spectra of N II and O III, the atoms of which are similarly constituted, but differ in nuclear charge.

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Further Investigations of the Spectrum of Singly-Ionised Carbon (*C II*).

By A. Fowler, D.Sc., F.R.S., Yarrow Research Professor of the Royal Society, and E. W. H. Selwyn, B.Sc., Imperial College, South Kensington.

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Introductory.

In a previous paper* it was shown that a considerable number of lines attributed to singly-ionised carbon (C^+ or C II) could be arranged in a regular system of doublet series, involving transitions of a single electron. Numerous lines which appeared to belong to C II remained unclassified, but further analysis of the spectrum has been greatly facilitated by subsequent theoretical developments. In accordance with Hund's theory, quartet as well as doublet terms are to be expected, and several of these additional terms have now been identified. The present communication gives an account of the newly classified lines, and includes improved measurements for some of the lines previously considered.

Observational Data.

The wave-lengths of most of the additional lines involved in the present discussion were determined in the course of the investigation of the doublet system. The sources included the spark between graphite poles in air, the spark in hydrogen, the arc *in vacuo*, and vacuum tubes of carbon dioxide. In the spark at atmospheric pressure, most of the lines are too diffuse for accurate measurement and wave-lengths were consequently determined chiefly from vacuum tubes. The vacuum tube spectra of oxygen under similar varied conditions served for the elimination of lines due to oxygen in the CO_2 spectra.

By comparing spectra produced under different conditions of pressure and strength of discharge, the lines representing successive stages of ionisation could be sorted out with considerable certainty. In many cases the assignment of lines to C II was confirmed by their behaviour in the spark in air, since lines representing the higher stages of ionisation do not appear on the less refrangible side of λ 2300 in this source. As previously observed by Lockyer, Baxandall and Butler, however, some of the lines of C III in this region are brought out when the carbon spark is passed in an atmosphere of hydrogen.†

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* A. Fowler, 'Roy. Soc. Proc.,' A, vol. 105, p. 299 (1924).

† 'Roy. Soc. Proc.,' A, vol. 82, p. 541 (1909).

In the spark spectrum, it may be noted, lines of carbon are readily distinguished from lines of nitrogen and oxygen by using a rather long spark gap, so that the carbon lines are localised near the electrodes while the gas-lines extend right across the gap.

An additional source which has been employed is the "vacuum spark" or "hot spark." In the ordinary region of observation this has been found to be about equivalent to the carbon spark in hydrogen, which, as already remarked, includes the more prominent lines of C III as well as lines of C II. Lines of C IV, in this region of the spectrum, are readily obtained in vacuum tubes, as first observed by Merton.* In the region of short wave-lengths a strong condensed spark in hydrogen has been found to give all the lines which have been recorded in the vacuum spark, and to exhibit the chief lines of C IV with as great a relative intensity as has been recorded by Millikan in the "hot spark." In vacuum tube spectra it is not uncommon to find the C IV doublet at λ 1550 of intensity similar to that of the C I triplet on its longer wave-length side, and in some photographs it has been found of much greater intensity. It appears that where vacuum tube observations are convenient, they should be of greater experimental value on account of their wide range and comparative ease of operation.

The most convenient source for observations of C II in the region of short wave-lengths is the vacuum arc; in this case the C I and C II lines are strongly developed, whilst only the more fundamental lines of C III appear with any considerable intensity, and even the "D" lines of C IV at λ 1550 are relatively feeble. As a comparative source, the carbon spark in hydrogen, with varying amounts of self-induction, provided useful confirmation of the classification of lines according to the different stages of ionisation; spectra ranging from predominant C I and C II to predominant C III and C IV were obtained in this way over the region λ 2000 to λ 1200, which is the limit when a fluorite window is interposed between the sparking tube and the slit of the vacuum spectrograph. With the vacuum arc as source, the fluorite window being removed, photographs have been taken as far as λ 800, some of them in the second and higher orders of the grating. The 1-metre concave grating in use was ruled at the National Physical Laboratory and gives extremely good definition and resolution—the C I triplet at λ 1561 is readily resolved into its three components in the first order—but no lines have been obtained of wave-length shorter than λ 800 with this instrument.

Important contributions to the investigation of the spectrum of C II have been made by Bowen in his classification and remarkably accurate measurements of lines in the extreme ultra-violet.* These measurements have been adopted so far as they go, and have been used as standards for additional determinations. Some of the lines which occur in the visible spectrum of C II have also been classified by C. Mihul,† in agreement with the results which had already been obtained in the course of the present investigation.

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* 'Roy. Soc. Proc.,' A, vol. 91, p. 498 (1915).

Most of the brighter lines in the region less refrangible than λ 2300 have been measured in the first order of a 10-foot grating and several of them in the third order. From λ 2300 to λ 3900 other lines were measured on photographs taken with Hilger's large quartz spectrograph (E.1) and from λ 3900 to λ 7300 with glass spectrographs of large dispersion. Some of the lines in the red which have been found to form multiplets, however, are very faint and the wave-lengths of such lines are probably subject to considerable errors. A specially adjusted quartz spectrograph by Bellingham and Stanley, obtained with the aid of the Government Grant Committee, has also been used for the region λ 1840 to λ 2300.

Predicted Terms.

Most of the terms of C II may be considered as arising from the addition of an electron, in various orbits, to a C III core. The configurations corresponding with the deepest terms of C III, and Bowen's term values are as follows :—

Configuration.				Terms.
1_1	2_1	2_2		
2	2		$1s^2\,2s^2$	$2s\,{}^1S_0$ 375463
2	1	1	$1s^2\,2s\,2p$	$2p\,{}^3P_1$ 331939 ; $2p\,{}^1P_1$ 273110

It should be remarked that while there are good grounds for the value assigned to $2p\,{}^3P_1$ the other values depend upon the identification of λ 2297 (ν 43524) with ${}^1S_0$—${}^3P_1$, and there is at present no confirmation of this assignment. The terms ${}^1S_0$ and ${}^1P_1$, however, are probably correct relatively to each other.

The series dealt with in the previous paper are derived by the addition of an electron to the core in its most stable state ($2s\,{}^1S$). The corresponding configurations and terms are shown under A in Table I, where the previous notation has been modernised as shown below :—

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* 'Phys. Rev.,' vol. 29, p. 231 (1927).

† 'C.R.,' vol. 184, p. 1648 (1927).

Previous notation.	Present notation.
2 (1) π_1	$2p\,^2P_2$
2 (1) π_2	$2p\,^2P_1$
3 (2) σ	$3s\,^2S_1$
3 (2) δ_1	$3d\,^2D_3$
3 (2) δ_2	$3d\,^2D_2$
4 (3) ϕ_1	$4f\,^2F_4$
4 (3) ϕ_2	$4f\,^2F_3$
x	$2p'\,^2S_1$

A second family of terms arises when the fifth electron is added to a C III core in the $2p\,^3P$ state. This includes quartet and doublet terms as shown under B in Table I. The terms of this group are conveniently distinguished by "priming" the electron symbols which are used as prefixes to the term symbols, as in previous papers.*

Other doublet terms, arising from the addition of an electron to a C III core in the $2p\,^1P$ state, are also possible. From $3s'$ downwards these would be similar in type to the doublet terms tabulated for the ^3P state of the core but none of these has been identified, and they are not included in the table.

Still another group of terms, as found by Bowen in the spectrum of the similarly constituted atoms of N III, corresponds to a displacement of both the 2_1 electrons to 2_2 orbits, as shown under C in Table I. The system of double primes which has become generally familiar does not appear to be completely applicable to this group, and the terms are accordingly distinguished by the prefix $2p^3$.

The combinations to be expected are indicated by the rules for electron transitions ; namely, $\Delta k = \pm 1$ for one electron, and, if there are simultaneous transitions of two electrons, $\Delta k = 0$ or 2 for the second ($k = 1, 2, 3, \ldots$ for $s, p, d, \ldots$). They are most conveniently shown by the diagram at the corner of the table, but it should be noted that combinations are further restricted by the selection rule for inner quantum numbers, *i.e.*, $\Delta j = \pm 1$ or 0, with $0 \rightarrow 0$ forbidden. Combinations of terms connected by broken lines are possible, but are unlikely to be of any great intensity.

In Table I the electron configurations are exhibited first in the usual tabular

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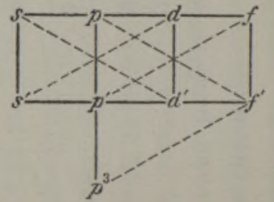
* 'Roy. Soc. Proc.,' A, vol. 117, p. 317 (1927), and vol. 118, p. 34 (1928).

Table I.—Predicted Terms of C II.

	K	L		M			N				O		Electrons outside rare gas shell.	Adopted prefix.	Terms.	*Combination Possibilities.*
	1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2				
A	2	2	1										$2s^2\ 2p$	$2p$	^2P	
	2	2		1									$2s^2\ 3s$	$3s$	^2S	
	2	2			1								$2s^2\ 3p$	$3p$	^2P	
	2	2				1							$2s^2\ 3d$	$3d$	^2D	
	2	2					1						$2s^2\ 4s$	$4s$	^2S	
	2	2						1					$2s^2\ 4p$	$4p$	^2P	
	2	2							1				$2s^2\ 4d$	$4d$	^2D	
	2	2								1			$2s^2\ 4f$	$4f$	^2F	
	2	2									1		$2s^2\ 5s$	$5s$	^2S	
B	2	1	2										$2s\ 2p^2$	$2p'$	^4P	$^2S\ ^2P\ ^2D$
	2	1	1	1									$2s\ 2p\ 3s$	$3s'$	^4P	^2P
	2	1	1		1								$2s\ 2p\ 3p$	$3p'$	$^4S\ ^4P\ ^4D$	$^2S\ ^2P\ ^2D$
	2	1	1			1							$2s\ 2p\ 3d$	$3d'$	$^4P\ ^4D\ ^4F$	$^2P\ ^2D\ ^2F$
	2	1	1				1						$2s\ 2p\ 4s$	$4s'$	^4P	^2P
	2	1	1					1					$2s\ 2p\ 4p$	$4p'$	$^4S\ ^4P\ ^4D$	$^2S\ ^2P\ ^2D$
	2	1	1						1				$2s\ 2p\ 4d$	$4d'$	$^4P\ ^4D\ ^4F$	$^2P\ ^2D\ ^2F$
	2	1	1							1			$2s\ 2p\ 4f$	$4f'$	$^4D\ ^4F\ ^4G$	$^2D\ ^2F\ ^2G$
C	2		3										$2p^3$	$2p^3$	^4S	$^2P\ ^2D$

form, and again, omitting electrons belonging to the completed rare gas shell, in a form which is more convenient for writing; *e.g.*, $2s^2\,2p$ means that there are two electrons in the $2s$ or 2_1 level, and one in the $2p$ or 2_2. Terms which have actually been identified are printed in heavy type. In addition, the combination $2p'\,{}^4\mathrm{P}—2p^3\,{}^4\mathrm{S}$ has been identified by Bowen, but the terms themselves have not yet been evaluated.

Doublet Term Values.

In the revision of the regular doublet terms, no sufficient reason has been found to change the original values, except those which depended upon measurements of lines in the extreme ultra-violet, for which more accurate determinations have since become available through the work of Bowen. Thus the terms $2p'\,{}^2\mathrm{S}_1$ (previously "x") $= 100164{\cdot}9$ and $3s\,{}^2\mathrm{S}_1 = 80121{\cdot}12$ have been retained and utilised for amending the value of $2p\ {}^2\mathrm{P}$, giving $2p\,{}^2\mathrm{P}_2 = 196595{\cdot}0$, $2p\,{}^2\mathrm{P}_1 = 196659{\cdot}0$. In deriving the $2p'\,{}^2\mathrm{P}$ terms from these the values have been slightly adjusted to accord with the $\Delta\nu$ more accurately determined from the combination $2p'\,{}^2\mathrm{P}—2p^3\,{}^2\mathrm{D}$. Higher doublet terms from the previous paper have been utilised for the identification of additional lines in the extreme ultra-violet; namely, $2p\,{}^2\mathrm{P}—5d$, $6d$, $7d\,{}^2\mathrm{D}$. The agreement between calculated and observed values is fairly satisfactory.

The $2p'$ doublet terms, and thence $2p^3\,{}^2\mathrm{D}$, it should be noted, have been determined from combinations with the main doublet terms, so that all the values assigned to doublet terms are in correct relation with each other. In other words, all these terms are referred to the limit ${}^1\mathrm{S}$ of the C III core.

The term $2p^3\,{}^2\mathrm{P}$ has not been identified; from the irregular doublet law, as applied to C II, N III and O IV, its value is estimated at about 25500, but corresponding combinations with $2p'$ doublet terms have not been certainly recognised.

Quartet Term Values.

There are three sequences of two terms each, from which the quartet terms can be calculated with reasonable accuracy by the use of the simple Rydberg formula. Thus, from the known differences of the respective pairs of terms, with $\mathrm{R} = 109737$, the following results are obtained:—

$\Delta\nu$		
42586	$3s'\,{}^4\mathrm{P}_1 = 82850$	
	$4s'\,{}^4\mathrm{P}_1 = 40264$	
31077	$3p'\,{}^4\mathrm{S}_2 = 64954$	$3s'\,{}^4\mathrm{P}_1—3p'\,{}^4\mathrm{S}_2 = 17896$
	$4p'\,{}^4\mathrm{S}_2 = 33877$	$3s'\,{}^4\mathrm{P}_1—3p'\,{}^4\mathrm{D}_1 = 14727$
33064	$3p'\,{}^4\mathrm{D}_1 = 68123$	
	$4p'\,{}^4\mathrm{D}_1 = 35059$	

If the calculated term values were entirely consistent, the differences shown on the right would have been equal to the observed lines $\nu = 17724$ and $\nu = 14730$ respectively. The deviations are not great, and the adoption of $3s\,^4P_1 = 82850$ will clearly provide a basis for quartet term values which is probably not far from exact. It should be mentioned, however, that the terms $3d'\,^4P_1$ and $4d'\,^4P_1$, with $\Delta\nu = 21963$, when treated in the same way, yield term values nearly 1100 units smaller than those given by the other pairs of terms.

The terms which have now been identified and evaluated are collected in Table II, where wave-number separations of multiple terms are also indicated. As already remarked, the value of the deep term $2p'\,^4P$ has not been found, for although Bowen has identified the combination $2p'\,^4P—2p^3\,^4S_2$ ($\nu = 98972$, etc.) neither of these terms has been recognised in other combinations. Hund's rule that of the terms arising from a given configuration, the one of highest multiplicity is usually the deepest, suggests that $2p^3\,^4S_2$ is greater than $2p^3\,^2D$ ($= 46196$), and consequently, since $2p'\,^4P_3—2p^3\,^4S_2 = 98973$, that $2p'\,^4P$ is greater than 145170. It is somewhat disappointing that the intercombination $2p\,^2P—2p'\,^4P$, representing the two deepest terms of the spectrum, has not been found. The corresponding lines would be expected to have wave-numbers less than 51425, and thus to occur in a part of the spectrum which has been well explored.

Table II.—Terms of C II.

(A.)

$2p\,^2P_1$	196659	*64·0*	$3s\,^2S_1$	80121·12	$3d\,^2D_2$	51109·01	*1·45*	$4f\,^2F_{34}$	27679·95
$^2P_2$	196595				$^2D_3$	51107·56			
			$4s\,^2S_1$	39424·57				$5f\,^2F_{34}$	17702·54
$3p\,^2P_1$	64934·32	*11·13*			$4d\,^2D_2$	28535·08	*0·41*		
$^2P_2$	64923·19		$5s\,^2S_1$	23310·82	$^2D_3$	28534·67		$6f\,^2F_{34}$	12282·80
$4p\,^2P_1$	34140·30	*5·92*			$5d\,^2D_3$	18164·2			
$^2P_2$	34134·38								
					$6d\,^2D_{23}$	[12558]			
					$7d\,^2D_{23}$	[9193]			

Table II (continued).

(B.)

†$2p'$	^4P	> 145170		$^2S_1$	100164·9		$^2P_1$ $^2P_2$	86033·9 85992·7	*41·2*	$^2D_3$ $^2D_2$	121728·1 121726·9	*1·2*
	$\Delta\nu$	*29 : 21*										
$3s'$	$^4P_1$ $^4P_2$ $^4P_2$	*82850·00 82826·24 82781·27	*23·76* *44·97*							(^2P)		
$3p'$	$^4S_2$	65126·01		$^4P_1$ $^4P_2$ $^4P_3$	63389·68 63373·38 63350·95	*16·30* *22·43*	$^4D_1$ $^4D_2$ $^4D_3$ $^4D_4$	68120·20 68105·50 68080·49 68044·22	*14·70* *25·01* *36·27*	^{2}(S P D)		
$3d'$	$^4P_3$ $^4P_2$ $^4P_1$	50972·7 50951·2 50937·0	*−21·5* *−14·2*	$^4D_1$ $^4D_2$ $^4D_3$ $^4D_4$	53258·5 53252·9 53244·2 53233·9	*5·6* *8·7* *10·3*	$^4F_2$ $^4F_3$ $^4F_4$ $^4F_5$	54063·9 54049·6 54030·0 54002·4	*14·3* *19·6* *27·6*	^{2}(P D F)		
$4s'$	$^4P_1$ $^4P_2$ $^4P_3$	40264·44 40240·42 40194·34	*24·02* *46·08*							(^2P)		
$4p'$	$^4S_2$	34049·1		^4P	[33100]		$^4D_1$ $^4D_2$ $^4D_3$ $^4D_4$	35056·4 35042·1 35020·1 34986·7	*14·3* *22·0* *33·4*	^{2}(S P D)		
$4d'$	$^4P_3$ $^4P_2$ $^4P_1$	29006·23 28985·73 28973·83	*−20·50* *−11·90*	^{4}(D F)						^{2}(P D F)		

(C.)

$2p^3$	$^4S_2$	> 46200		^2P	[25500]		$^2D_3$ $^2D_2$	46196·2 46191·1	*−5·1*

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* Calculated by Rydberg formula as basis of quartet terms.

† The $2p'$ term values are referred to the ^1S limit, while the other terms of group B are referred to ^3P.

The above estimate of the value of $2p'$ ^4P, it should be noted, is referred to the ^1S state of the C III core, and, following a suggestion made by Prof. H. N. Russell, the term might be written in the form $2p'$ (^1S) ^4P. Its value referred to the ^3P state, or $2p'$ (^3P) ^4P, which would be expected to be in Rydberg sequence with $3p'$ ^4P, would be greater than this by the difference $^1S_0$—$^3P_1$ of C III. Bowen has taken this to be 43524 (representing the supposed C III " resonance " line λ 2297) and assuming this to be correct, the value of $2p'$ ^4P referred to the ^3P limit would be $>$ (145170 + 43524), or $>$ 188694. In view of its great intensity, however, it is possible that λ 2297 may not be the resonance line of C III, and that a line of higher wave-number should have been selected. The order of magnitude is, nevertheless, generally confirmed by a comparison of the doublet p P and quartet p' P terms, from which it may be inferred that $2p'\ ^4P$, referred to the ^3P limit of C III, is probably not much smaller 196595. A value of, say, 193000 would not be inconsistent with the values assigned to $3p'\ ^4P$ and $4p'\ ^4P$.

Thus, in searching for combinations between the doublet terms of groups A and C with the quartet and doublet terms of group B, the latter (except the $2p'$ terms which are already evaluated with reference to the ^1S limit) must be reduced by an amount representing $^1S_0$—$^3P_1$ of the C III spectrum. Attempts to trace such combinations, however, assuming alternative possible identifications of the resonance line of C III, have so far been unsuccessful.

Doublet Combinations.

The doublet combinations which have been identified are collected in Table III. This includes all the lines considered in the previous paper, and additional lines which have been identified by Bowen and the authors. For lines in the extreme ultra-violet which have not yet been measured with great accuracy the calculated wave-numbers, enclosed in square brackets, are indicated for comparison with the values corresponding with the observed wave-lengths. Other calculated lines are also distinguished by brackets.

Quartet Combinations.

The quartet combinations which have been identified are collected in Table IV.

Unclassified Lines.

Among the unclassified lines are two complex doublets which may possibly involve doublet terms of group B, none of which beyond the first row ($2p'$) has yet been evaluated. These may be represented as follows :—

? $3s'$	$^2P_2$		$^2P_1$
? $3p'\ ^2D_2$	16381·95 (1)	*19·48*	16401·43 (3)
	10·75		
$^2D_3$	16392·70 (5)		

? $4d'$	$^2P_2$		$^2P_1$
? $3p'\ ^2D_2$	37854·2 (1)	*5·0*	37859·2 (2)
	7·3		
$^2D_3$	37846·9 (3)		

There is also an unclassified pair λλ 3167·95 (3), 3165·51 (4), Δν 24·33, which is notable for the sharpness of its lines.

	$2p\,{}^2P_2$ 196595·0	*64·0*	$2p\,{}^2P_1$ 196659·0	$3p\,{}^2P_2$ 64923·19	*11·13*	$3p\,{}^2P_1$ 64934·32	$4p\,{}^2P_2$ 34134·38	*5·92*	$4p\,{}^2P_1$ 34140·30	$4f\,{}^2F_{43}$ 27679·95	$5f\,{}^2F_{45}$ 17702·54	$6f\,{}^2F_{43}$ 12282·80
$2p'\,{}^4P > 145170$	[<51425]											
$2p'\,{}^2D_2 = 121726{\cdot}9$ $2p'\,{}^2D_3 = 121728{\cdot}1$	 *74866·9 (10)		74932·1 (8)	 *56804·0 (2)		56790·8 (1)	 *87595·6 (2)			 [94048]	 [104026]	 [109445]
$2p'\,{}^2S_1 = 100164{\cdot}9$	*96430 (6)	*63·7*	96493·8 (6)	35241·75 (10)	*11·06*	35230·69 (8)	[66030·5]					
$2p'\,{}^2P_1 = 86033{\cdot}9$	*110561·7 (7)	*62·7*	110624·4 (8)									
	41·5		*41·6*									
$2p'\,{}^2P_2 = 85992{\cdot}7$	110603·2 (8)	*62·8*	110666·0 (7)	[21069·5]			[51858·5]					
$3s\ {}^2S_1 = 80121{\cdot}12$	*116474·0 (6)	*64·2*	116538·2 (5)	15197·93 (10)	*11·13*	15186·80 (8)	45986·74 (2)	*5·92*	45980·82 (1)			
$3d\ {}^2D_2 = 51109{\cdot}01$ $3d\ {}^2D_3 = 51107{\cdot}56$	[145486] [145487] *145486·1 (5)	 *63·1*	[145550·0] 145549·2 (5)	[13814·18] 13815·63 (8)		13825·31 (6)	[16974·63] 16973·32 (3)		16968·48 (2)	23428·99 (8) 23427·61 (10)	33405·71 (4)	38825·45 (1)
$4s\ {}^2S_1 = 39424{\cdot}57$	[157170] †157183 (1)		[157234]	25498·65 (8)	*11·06*	25509·71 (6)	§					
$4d\ {}^2D_2 = 28535{\cdot}08$ $4d\ {}^2D_3 = 28534{\cdot}67$	[168060] *168062 (2)		[168124] 168127 (2)	[36388·11] 36388·52 (6)		36399·24 (5)	§			§		[16252]
$5s\ {}^2S_1 = 23310{\cdot}82$	[173284] †173190 (1)		[173348]	41612·37 (2)	*10·90*	41623·27 (1)	§					
$5d\,{}^2D_{32} = 18164{\cdot}2$	[178431] †178412		[178495]	46759·34 (1)	*10·50*	46769·84 (1)	[15970·2]			§	§	§
$6d\,{}^2D_{32} = [12558]$	[184037] †184026 (2)		[184101]	[52365]			[21576]			[15122]	§	§
$7d\,{}^2D_{32} = [9193]$	187402 †187546 (1)		[187466]	[55730]			[24941]			[18487]	§	§

* Measurements and classification by Bowen. † Observations by Lang; all but 173190 observed also by Millikan and by Simeon. § Out of range.

	$2p^3\,{}^2D_3$ 46196·2	*−5·1*	$2p^3\,{}^2D_2$ 46191·1
$2p'\,{}^4P > 145170$	[>98974]		
$2p'\,{}^2D_3 = 121728{\cdot}1$	[75531·9]		[75537·0]
−1·2			
$2p'\,{}^2D_2 = 121726{\cdot}9$	[75530·7] 75531·0(7)		[75535·8]
$2p'\,{}^2P_1 = 86033{\cdot}9$			39842·77(8)
41·2			*41·24*
$2p'\,{}^2P_2 = 85992{\cdot}7$	39796·46(10)	*5·07*	39801·53(4)

Table IV.—Quartet Combinations of C II.

	$3s'\,^4P_3$ 82781·27	*44·97*	P_2 82826·24	*23·76*	P_1 82850·00	$4s'\,^4P_3$ 40194·34	*46·08*	P_2 40240·42	*24·02*	P_1 40264·44	$3d'\,^4P_3$ 50972·7	*−21·5*	$^4P_2$ 50951·2	*−14·2*	P_1 50937·0
$3p'\,^4D_1$ = 68120·20			14706·06 (0)	*23·73*	14729·79 (2)			27879·62 (2)	*23·86*	27855·76 (1)			[17169·0]		17183·7 (0)
14·70			*14·61*		*14·82*			*14·38*		*(15·27)*					*15·5*
D_2 = 68105·50	14675·72 (0)	*44·95*	14720·67 (3)	*23·94*	14744·61 (2)	[27911·1]		27865·24 (2)	*(24·77)*	*27840·49 (2)	[17132·8]		17154·4 (1)	*13·8*	17168·2 (0)
25·01	*25·03*		*25·10*					*(24·75)*					*25·0*		
D_3 = 68080·49	14700·75 (3)	*45·02*	14745·77 (4)			27886·23 (1)	*(45·74)*	*27840·49 (2)			17107·5 (0)	*21·9*	17129·4 (1)		
36·27	*36·30*					*36·43*					*36·0*				
D_4 = 68044·22	14737·05 (6)					27849·80 (4)					17071·5 (2)				
$3p'\,^4S_2$ = 65126·01	17655·13 (4)	*45·10*	17700·23 (3)	*23·89*	17724·12 (2)	24931·26 (2)	*45·74*	24885·52 (1)	*23·89*	24861·63 (0)	14153·6 (1)	*21·1*	14174·7 (1)	*14·2*	14188·9 (0)
$3p'\,^4P_1$ = 63389·68			19436·65 (2)	*23·57*	19460·22 (0)										
16·30			*16·19*		*16·30*										
P_2 = 63373·38	19408·01 (3)	*44·83*	19452·84 (1)	*23·68*	19476·52 (3)										
22·43	*22·33*		*22·43*												
P_3 = 63350·95	19430·34 (5)	*44·93*	19475·27 (3)			[23157]					§				
$4p'\,^4S_2$ = 34049·1	[48732]					§					16923·4 (1)	*21·7*	16901·7 (0)	*13·3*	16888·4 (0)

	$3d'\,^4D_4$ 53233·9	*10·3*	D_3 53244·2	*8·7*	D_2 53252·9	*5·6*	D_1 53258·5	$3d'\,^4F_5$ 54002·4	*27·6*	F_4 54030·0	*19·6*	F_3 54049·6	*14·3*	F_2 54063·9
$3p'\,^4D_1$ = 68120·20					[14867·3]		14861·7 (0)							†14056·2 (1)
14·70							*(14·8)*							*14·0*
D_2 = 68105·50			†14861·7 (0)	*(9·1)*	14852·6 (0)	*(5·7)*	*14846·9 (0)					†14056·2 (1)	*(14·0)*	*14042·2 (2)
25·01			*25·10*		*24·4*							*(25·9)*		
D_3 = 68080·49	*14846·9 (0)	*(10·6)*	14836·3 (0)	*(8·1)*	14828·2 (0)					14050·7 (1)	*20·4*	14030·3 (0)		[14017]
36·27	*(36·6)*		*36·0*							*36·2*				
D_4 = 68044·22	14810·3 (2)	*10·0*	14800·3 (0)					*14042·2 (2)	*(27·7)*	14014·5 (0)				
$4p'\,^4D_1$ = 35056·4														†19007·5 (3)
14·3														
D_2 = 35042·1												†19007·5 (3)		[19022]
22·0												*(22·0)*		
D_3 = 35020·1										†19007·5 (3)	*(22·0)*	19029·5 (1)	*(14·9)*	*19044·4 (0)
33·4										*(36·9)*				
D_4 = 34986·7	18248 (0)							19015·7 (2)	*(28·7)*	*19044·4 (0)				

$2p'\,^4P_3 - 2p^3\,^4S_2$ = 98972·5 (6)
28·6
P_2 S_2 = 99001·1 (6)
21·5
P_1 S_2 = 99022·6 (5)
$2p^3\,^4S_2 > 46196$

$3p'\,^4S_2 - 4d'\,^4P_3$ = 36119·78(2)
—20·50
S_2 P_2 = 36140·28(1)
−11·90
S_2 P_1 = 36152·18(0)
$4d'\,^4P_3$ = 29006·23

*† Used more than once.
§ Out of range.

Catalogue of Lines attributed to C II.

Table V is a catalogue of all the lines between λ 7236 and λ 2137 which have appeared to be attributable to C II. The wave-lengths, followed by numbers in brackets representing rough estimates of intensity, are given in the first column, the corresponding wave-numbers in the second, and the classification, where ascertained, in the third column.

Table V.—List of C II Lines, λ 7236—λ 2137.

λ.	ν.	
37]	[13814·18]	$3p\ {}^2P_2 — 3d\ {}^2D_2$
36·19 (8*n*)	13815·63	$P_2\quad D_3$
31·12 (6*n*)	13825·31	$P_1\quad D_2$
39·68 (00)	14002·39	
33·52 (0)	14014·47	$3p'\ {}^4D_4 — 3d'\ {}^4F_4$
25·49 (0)	14030·26	$D_3\quad F_3$
19·4$_5$ (2)	14042·16	$\begin{cases} D_4 & F_5 \\ D_2 & F_2 \end{cases}$
15·13 (2–)	14050·69	$D_3\quad F_4$
12·36 (1)	14056·16	$\begin{cases} D_2 & F_3 \\ D_1 & F_2 \end{cases}$
63·4 (1*n*)	14153·6	$3p'\ {}^4S_2 — 3d'\ {}^4P_3$
52·9 (1*n*)	14174·7	$S_2\quad P_2$
45·8 (0*n*)	14188·9	$S_2\quad P_1$
812·19 (0)	14675·72	$3s'\ {}^4P_3 — 3p'\ {}^4D_2$
00·50 (3)	14700·75	$P_3\quad D_3$
798·04 (1)	14706·06	$P_2\quad D_1$
791·30 (3)	14720·67	$P_2\quad D_2$
787·09 (2)	14729·79	$P_1\quad D_1$
783·75 (6)	14737·05	$P_3\quad D_4$
780·27 (2)	14744·61	$P_1\quad D_2$
779·74 (4)	14745·77	$P_2\quad D_3$
754·75 (0)	14800·32	$3p'\ {}^4D_4 — 3d'\ {}^4D_3$
750·22 (2)	14810·25	$D_4\quad D_4$
742·05 (0)	14828·20	$D_3\quad D_2$
738·36 (1)	14836·32	$D_3\quad D_3$
733·56 (0)	14846·89	$\begin{cases} D_3 & D_4 \\ D_2 & D_1 \end{cases}$
6730·79 (0)	14852·59	$D_2\quad D_2$
6726·84 (0)	14861·73	$\begin{cases} D_2 & D_3 \\ D_1 & D_1 \end{cases}$
6721·67 (0)	14873·17	
6707·60 (0)	14904·35	
6582·85 (8)	15186·80	$3s\ {}^2S_1 — 3p\ {}^2P_1$
6578·03 (10)	15197·93	$S_1\quad P_2$
*6243·98 (0)	16011·02	
*6115·21 (0)	16348·15	
6102·59 (0)	16381·95	
6098·62 (3)	16392·70	
6095·37 (2)	16401·43	
5919·60 (0)	16888·4	$3d'\ {}^4P_1 — 4p'\ {}^4S_1$
5914·92 (0)	16901·7	$P_2\quad S_1$
5907·36 (1)	16923·4	$P_3\quad S_1$
5891·65 (3)	16968·48	$3d\ {}^2D_2 — 4p\ {}^2P_1$
5889·97 (5)	16973·32	$D_3\quad P_2$
[5889·5]	[16974·6]	$D_2\quad P_2$
5856·09 (2)	17071·5	$3p'\ {}^4D_4 — 3d'\ {}^4P_3$
5843·77 (0)	17107·5	$D_3\quad P_3$
5836·31 (1)	17129·4	$D_3\quad P_2$
5827·80 (1)	17154·4	$D_2\quad P_2$
5823·13 (0)	17168·2	$D_2\quad P_1$
5817·87 (0)	17183·7	$D_1\quad P_1$
5662·51 (4)	17655·13	$3s'\ {}^4P_3 — 3p'\ {}^4S_2$
5648·08 (3)	17700·23	$P_2\quad S_2$
5640·50 (2)	17724·12	$P_1\quad S_2$
5478·6 (0)	18248	$3d'\ {}^4D_4 — 4p'\ {}^4D_4$
5272·56 (1)	18961·4	
5259·62 (3)	19007·5	$3d' \begin{cases} {}^4F_4 \\ F_3 \\ F_2 \end{cases} — 4p' \begin{cases} {}^4D_3 \\ D_2 \\ D_1 \end{cases}$
5257·36 (2)	19015·7	$F_5\quad D_4$
5253·55 (1)	19029·5	$F_3\quad D_3$
5249·43 (0)	19044·4	$F_4\quad D_4$

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* Merrill (private communication).

Table V—continued.

λ.	ν.	
5151·08 (3*d* ?)	19408·01	$3s' \, {}^4P_3 - 3p' \, {}^4P_2$
5145·16 (5)	19430·34	$P_3 \quad P_3$
5143·49 (2)	19436·65	$P_2 \quad P_1$
5139·21 (1)	19452·84	$P_2 \quad P_2$
5137·26 (0)	19460·22	$P_1 \quad P_1$
5133·29 (2)	19475·27	$P_2 \quad P_3$
5132·96 (3)	19476·52	$P_1 \quad P_2$
5121·69 (0)	19520·1	
5119·55 (1)	19527·6	
5114·07 (1)	19548·5	
4964·90 (1)	20135·8	
4618·85 (2*d* ?)	21644·3	
4411·52 (2)	22661·58	
4411·20 (2)	22663·22	
4410·06 (1)	22669·08	
4374·28 (2)	22854·50	
4372·49 (1)	22863·87	
4371·59 (0)	22868·57	
4267·27 (10)	23427·61	$3d \, {}^2D_3 - 4f \, {}^2F_{43}$
4267·02 (8)	23428·99	$D_2 \quad F_3$
4074·89 (1)	24533·70	
4074·53 (2)	24535·80	
4070·30 (3)	24561·30	C II ?
4068·97 (3)	24569·33	
4021·13 (0)	24861·63	$3p' \, {}^4S_2 - 4s' \, {}^4P_1$
4017·27 (1)	24885·52	$S_2 \quad P_2$
4009·90 (2)	24931·26	$S_2 \quad P_3$
3980·35 (2)	25116·34	
3952·08 (1)	25296·00	
3920·677 (8)	25498·65	$2p \, {}^2P_2 - 2s \, {}^2S_1$
3918·977 (6)	25509·71	$P_1 \quad S_1$
3889·18 (1)	25705·10	
3885·99 (0)	25726·21	
3876·670 (1)	25788·05	
3876·409 (2)	25789·79	
3876·188 (4)	25791·26	
3876·051 (1)	25792·17	
3590·87 (2)	27840·49	$3p' \left\{ \begin{matrix} {}^4D_3 \\ D_2 \end{matrix} \right. - 4s' \left\{ \begin{matrix} {}^4P_2 \\ P_1 \end{matrix} \right.$
3589·67 (4)	27849·80	$D_4 \quad P_3$
3588·92 (1)	27855·61	$D_1 \quad P_1$
3587·68 (2)	27865·24	$D_2 \quad P_2$
3585·83 (2)	27879·62	$D_1 \quad P_2$
3584·98 (1)	27886·23	$D_3 \quad P_3$
3361·75 (1)	29737·90	
3361·09 (2)	29743·74	
3167·95 (3)	31557·05	
3165·51 (4)	31581·38	
2992·63 (4)	33405·71	$3d \, {}^2D_{32} - 5f \, {}^2F_{43}$
2967·91 (3)	33683·93	
2967·31 (2)	33690·75	
2885·47 (2*n*)	34646·26	
2837·602 (8)	35230·69	$2p' \, {}^2S_1 - 2p \, {}^2P_1$
2836·710 (10)	35241·75	$S_1 \quad P_2$
2801·36 (2*n*)	35686·45	
2767·75 (2)	36119·78	$3p' \, {}^4S_2 - 4d' \, {}^4P_3$
3766·18 (1)	36140·28	$S_2 \quad P_2$
2765·27 (0)	36152·18	$S_2 \quad P_1$
[2747·34]	[36388·1]	$2p \, {}^2P_2 - 2d \, {}^2D_2$
2747·31 (6)	36388·52	$P_2 \quad D_1$
2746·50 (4)	36399·24	$P_1 \quad D_2$
2725·90 (1)	36674·3	
2725·29 (1)	36682·5	
2724·87 (0)	36688·1	
2641·44 (3)	37846·88	
2640·93 (1)	37854·18	
2640·58 (2)	37859·20	
2595·07 (1*n*)	38523·1	
2592·00 (2*n*)	38568·7	
2574·86 (1*n*)	38825·5	$3d \, {}^2D_{32} - 6f \, {}^2F_{43}$
2512·03 (8)	39796·46	$2p' \, {}^2P_2 - 2p^3 \, {}^2D_3$
2511·71 (4)	39801·53	$P_2 \quad D_2$
2509·11 (7)	39842·77	$P_1 \quad D_2$
2402·40 (2)	41612·37	$3p \, {}^2P_2 - 5s \, {}^2S_1$
2401·77 (1)	41623·27	$P_1 \quad S_1$
2191·37 (2)	45619·3	
2177·66 (1)	45906·4	
2174·14 (1)	45980·82	$3s \, {}^2S_1 - 4p \, {}^2P_1$
2173·86 (2)	45986·74	$S_1 \quad P_2$
2163·60 (5)	46204·7	
2137·93 (2)	46759·34	$3p \, {}^2P_2 - 5d \, {}^2D_{32}$
2137·45 (1)	46769·84	$P_1 \quad D_2$

Table VI is a list of carbon lines which have been observed between λ 2137 and λ 1894; the distinction between C II and C III by experimental behaviour is somewhat difficult in this region, but suggested or known origins are indicated.

Table VI.—Lines of Carbon between λ 2137 and λ 1894.

λ_{air}.	ν.	
2092·40 (4)	47776·8	C III ?
2016·92 (1*d* ?)	49564·5	,,
2010·18 (5)	49730·6	,,
2009·67 (4)	49743·3	,,
λ_{vac}.		
1988·05 (1)	50300·5	C II ?
1979·79 (3)	50510·4	C III ?
1979·35 (4)	50521·6	,,
1931·03 (10)	51785·9	C I
1923·52 (4*d* ?)	51988·0	} C III
1923·13 (5)	51998·6	
1894·49 (2)	52784·6	C III ?

Table VII includes lines of carbon below λ 1760 which have been classified as part of the C II spectrum. All of these occur in the vacuum arc, in

Table VII.—Classified Lines of C II λ 1760—λ 534.

λ_{vac}	ν		λ_{vac}.	ν	
1760·85 (2)	56790·8	$2p'\ {}^2D_2—3p\ {}^2P_1$	*858·561 (1)	116474·0	$2p\ {}^2P_2—3s\ {}^2S_1$
1760·44 (3)	56804·0	D_3 P_2	858·088 (0)	116538·2	P_1 S_1
1335·703 (10)	74866·9	$2p\ {}^2P_2—2p'\ {}^2D_3$	*687·351 (5)	145486·1	$2p\ {}^2P_2—3d\ {}^2D_3$
1334·541 (10)	74932·1	P_1 D_2	687·053 (5)	145549·2	P_1 D_2
1323·96 (7)	75531·0	$2p'\ {}^2D_{32}—2p^3\ {}^2D_{32}$	†636·2 (2)	157183	$2p\ {}^2P_{21}—4s\ {}^2S_1$
1141·61 (2)	87595·6	$2p'\ {}^2D_{32}—4p\ {}^2P_{21}$	*595·02 (2)	168062	$2p\ {}^2P_2—4d\ {}^2D_3$
1037·021 (7)	96430·1	$2p\ {}^2P_2—2p'\ {}^2S_1$	594·79 (2)	168127	P_1 D_2
1036·336 (5)	96493·8	P_1 S_1	†560·5 (2)	178412	$2p\ {}^2P_{21}—5d\ {}^2D_{32}$
*1010·382 (3)	98972·5	$2p'\ {}^4P_3—2p^3\ {}^4S_2$	†543·4 (1)	184026	$2p\ {}^2P_{21}—6d\ {}^2D_{32}$
1010·090 (3)	99001·1	P_2 S_2	†533·5 (1)	187441	$2p\ {}^2P_{21}—7d\ {}^2D_{32}$
1009·870 (5)	99022·6	P_1 S_2			
*904·472 (2)	110561·7	$2p\ {}^2P_2—2p'\ {}^2P_1$			
904·133 (2)	110603·2	P_2 P_2			
903·960 (2)	110624·4	P_1 P_1			
903·620 (2)	110666·0	P_1 P_2			

* λ and classification by Bowen ('Phys. Rev.,' vol. 29, p. 233 (1927)).
† Mean λ, Millikan, Simeon, and Lang.

company with lines of C I. Other observations of the vacuum arc have been made by Simeon,* and of the vacuum spark by Millikan and Bowen† and by Lang.‡ Wave-lengths and classification of lines of C I have been given in a previous paper.§

Summary.

The paper gives the results of a further investigation of the spectrum of singly-ionised carbon (C II) as observed over a wide range in various sources. Previous results for the regular doublet system have been revised, and numerous lines have been classified in the quartet system which is predicted by Hund's theory. A catalogue of all the lines which appear to be attributable to C II in the region λ 7200 to λ 2137 is included, and also a list of classified lines of shorter wave-length.

One of the authors (E. W. H. S.) is indebted to the Department of Scientific and Industrial Research for a grant which has enabled him to take part in this investigation.

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* 'Roy. Soc. Proc.,' A, vol. 102, p. 484 (1922), and vol. 104, p. 368 (1923).

† 'Phys. Rev.,' vol. 23, p. 8 (1924), and other papers.

‡ 'Phil. Trans.,' A, vol. 224, p. 377 (1924).

§ 'Roy. Soc. Proc.,' A, vol. 118, p. 34 (1928).

The Arc Spectrum of Silicon.

By A. Fowler, D.Sc., F.R.S., Yarrow Research Professor of the Royal Society.

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[Plate 18.]

Introductory.

In the Bakerian Lecture for 1924* it was shown that the changes in the spectrum of silicon which accompany increased energy of excitation represent successive stages of ionisation of the silicon atom. Besides the spectrum of the neutral atom (Si I), characterised by the series constant R, three other spectra were identified as Si II, Si III and Si IV, for which the series constant was 4R, 9R and 16R respectively, in accordance with Bohr's theory.

In view of the great advances in the theoretical interpretation of spectra which have since been made, it has seemed desirable to undertake a revision and extension of the earlier analyses of these spectra. The present communication gives an account of additional observational data for Si I and of the progress which has been made in the identification of the terms predicted for this spectrum by the theory of Heisenberg and Hund.

Observational Data.

The region of the arc spectrum considered in the previous paper extended from the visible spectrum to the beginning of the Schumann region about λ 1840. It was pointed out, however, that since the first triplet combinations occur in the ultra-violet, beginning at λ 2528, any additional members in sequence with them must be situated in the Schumann region. The arc spectrum in this region has accordingly been further investigated with the vacuum grating spectrograph.

In order to extend the observations as far as possible to short wave-lengths, and to minimise the introduction of lines of Si II, which appear conspicuously in the vacuum arc, the arc was passed in nitrogen at atmospheric pressure. It is known from observations in the ordinary parts of the spectrum that the substitution of nitrogen for air does not affect the spectrum of an arc, but for the present purpose nitrogen has the advantage of being transparent for short wave-lengths, whereas oxygen is strongly absorbent. Spectra obtained with an arc in nitrogen at atmospheric pressure are thus equivalent, as regards existing energy, to those given by an arc in air under ordinary conditions.

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* 'Phil. Trans.,' A, vol. 225, p. 36 (1924).

In work with the vacuum spectrograph it is usually an advantage to place the source as near as possible to the slit, and so, instead of putting the arc in a closed vessel, it was brought within about an inch from the slit and a slow stream of nitrogen passed between the slit and the arc. The slit was covered with a fluorite plate, and a short length of water-cooled brass tube extended from the slit towards the arc. Nitrogen was admitted through a side tube. In this way, photographs of the arc spectrum extending to about λ 1600, and sometimes further, were obtained. Two pairs of lines due to Si II appeared on some of the plates, but not on all of them, and, as in the visible spectrum, it appears that such lines were practically confined to the immediate neighbourhood of the poles.

Most of the photographs were taken in the first order of a grating having 15,000 lines per inch, which was ruled at the National Physical Laboratory. The definition and resolution given by this grating are excellent, as may be gathered from the enlarged copies which are reproduced in Plate 18. At a late stage of the investigation, another grating having 30,000 lines per inch, ruled on glass, became available through the kindness of Prof. R. W. Wood. A few photographs of the silicon arc spectrum have been taken with this second grating, and in these also the definition is very good; the additional dispersion and resolution on these plates have materially improved some of the data.

Pole pieces of elementary silicon yielded the most complete spectra, but good photographs were also obtained with potassium fluo-silicate on poles of Acheson graphite. The latter photographs were especially valuable because they included lines of carbon, most of which have been accurately measured by Bowen.* With poles of silicon, carbon was only represented by a trace of the very strong arc line at λ 1931. The photographs of the fluo-silicate spectrum were also of assistance in the classification of some of the singlets which occur in the Si I spectrum; it was found, for example, that while the singlet DF series appeared with undiminished strength in the fluo-silicate spectrum, the singlet DD series was relatively much reduced in intensity and extent.

As the silicon used in these experiments was known to be somewhat impure, the arc spectra of numerous other elements were photographed under similar conditions for purposes of comparison. A few lines of aluminium, including some of Al II, and a line of calcium were thus identified as arising from impurities. The pair of nitrogen lines, λλ 1745·26, 1742·74, also appeared conspicuously in most of the arc spectra.

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* 'Phys. Rev.,' vol. 29, p. 238 (1927).

Determination of Wave-lengths.

The photographs of the spectrum of potassium fluo-silicate were first carefully measured, and the wave-lengths of numerous silicon lines were obtained by interpolation with respect to the lines of carbon* and nitrogen. The most suitable lines among these were then used as standards for the reduction of the plates showing silicon lines alone. A valuable check on the values obtained for several of the silicon lines was, fortunately, provided by the analysis of the spectrum. As will be seen from Table III, a number of silicon lines which occur in the Schumann region can be calculated with great precision from the accurate values already determined for lines in the ordinary ultra-violet region. Lines on the first four rows of this table being used for the determination of the differences between the terms shown at the head, it is only necessary to add these differences to the wave numbers of some of the singlets which appear on the right in order to obtain the wave-numbers of associated lines in the Schumann region. When there could be no doubt as to the identity of calculated and observed wave-numbers the calculated values were adopted for tabulation. Such calculated wave-numbers are distinguished in Tables I and III by an asterisk; they may conveniently be collected as below, as good standards in the Schumann region are not yet very numerous.

ν.	λ_{vac}.	λ_{air}.	ν.	λ_{vac}.
47088·00	2123·683	2123·009	54090·11	1848·768
47128·14	2121·874	2121·200	54236·19	1843·788
47274·22	2115·318	2114·646	54313·25	1841·171
48014·58	2082·701	2082·035	54647·48	1829·910
48571·95	2058·801	2058·139	54793·56	1825·032
52503·29	1904·643		54870·62	1822·469
53138·25	1881·883		58578·82	1707·102
53163·53	1880·988		58724·90	1702·855
53309·61	1875·835		58801·96	1700·623
53386·67	1873·127			

An examination of the multiplets on which the above values depend, however, shows that the positions of the parent lines are not yet known with the greatest attainable accuracy, and to this extent the above values are to be considered provisional, though the errors are unlikely much to exceed one-hundredth of an angstrom.

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* Bowen's value for the carbon line, 1931·027, was replaced by 1930·95, deduced during the present investigation.

Catalogue of Silicon Arc Lines.

A general catalogue of silicon arc lines is given in Table I. The first column gives the wave-lengths and intensities, the wave-lengths to λ 2000 being in

Table I.—Arc Lines of Silicon.

λ_{air} (Int.).	ν.	Classification.
†11231·0 (8)	8902	$4s\,^1P_1-4p\,^1S_0$
†9867·7 (5)	10131	$4s\,^3P_1-4p\,^1S_0$
†9755·8 (10)	10248	$4p\,^1D_2-3d\,^1F_3$?
5948·552 (5)	16806·17	$4s\,^1P_1-5p\,^1S_0$
5797·869 (3)	17242·94	$4s\,^3P_2-5p\,^3D_3$?
5793·083 (2)	17257·19	$4s\,^3P_1-5p\,^3D_2$?
5780·390 (0)	17295·08	
5772·152 (1)	17319·77	$4s\,^3P_0-5p\,^3D_1$?
5754·240 (0)	17373·68	$4s\,^3P_2-5p\,^3P_1$
5708·408 (5)	17513·17	$P_2 \quad P_2$
5701·111 (1)	17535·58	$P_1 \quad P_0$
5690·435 (2)	17568·49	$P_1 \quad P_1$
5684·496 (3)	17586·84	
5665·566 (1)	17645·61	$P_0 \quad P_1$
5645·621 (1)	17707·94	$P_1 \quad P_2$
4102·945 (5)	24365·89	$3p\,^1S_0-4s\,^3P_1$
3905·534 (10)	25597·47	$3p\,^1S_0-4s\,^1P_1$
3020·01 (0)	33102·85	Si ?
2987·650 (5)	33461·39	$3p\,^1D_2-4s\,^3P_1$
2970·35 (2)	33656·27	$3p\,^1D_2-4s\,^3P_2$
2881·585 (10)	34692·97	$3p\,^1D_2-4s\,^1P_1$
2631·310 (5)	37992·57	$3p\,^1S_0-3d\,^1P_1$
2568·66 (2)	38919·15	$3p\,^1S_0-5s\,^3P_1$
2532·39 (2)	39476·52	$3p\,^1S_0-5s\,^1P_1$
2528·516 (10R)	39537·01	$3p^3\,P_2-4s\,^3P_1$
2524·118 (9R)	39605·89	$P_1 \quad P_0$
2519·210 (8R)	39683·03	$P_1 \quad P_1$
2516·123 (15R)	39731·73	$P_2 \quad P_2$
2514·331 (7R)	39760·04	$P_0 \quad P_1$
2506·904 (10R)	39877·83	$P_1 \quad P_2$
2452·136 (3)	40768·42	$3p\,^3P_2-4s\,^1P_1$
2443·378 (3)	40914·54	$P_1 \quad P_1$
2438·782 (3)	40991·64	$P_0 \quad P_1$
2435·159 (8R)	41052·61	$3p\,^1D_2-3p'\,^1D_2$
2303·02 (2)	43407·86	$3p\,^1S_0-4d\,^1P_1$
‡2289·60 (1)	43662·15	
‡2278·22 (0)	43880·44	$3p\,^1S_0-6s\,^3P_1$
‡2259·57 (1)	44242·48	$3p\,^1S_0-6s\,^1P_1$
2218·917 (1)	45052·96	$3p\,^3P_2-3p'\,^3D_1$
2218·080 (2)	45069·96	$P_2 \quad D_2$
2216·685 (4)	45098·32	$P_2 \quad D_3$
2211·750 (2)	45198·92	$P_1 \quad D_1$
2210·912 (3)	45216·07	$P_1 \quad D_2$
2207·980 (2)	45276·09	$P_0 \quad D_1$
2124·150 (10R)	47062·72	$3p\,^1D_2-3d\,^1F_3$
*2123·009 (2)	47088·00	$3p\,^1D_2-3d\,^1P_1$
*2121·200 (1)	47128·14	$3p\,^3P_2-3p'\,^1D_2$
*2114·646 (0)	47274·22	$3\rho\,^3P_1-3p'\,^1D_2$
2084·40 (2)	47960·09	$3p\,^1D_2-3d\,^1D_2$
*2082·035 (1)	48014·58	$3p\,^1D_2-5s\,^3P_1$
2065·48 (0)	48399·36	
2061·12 (1)	48501·73	
*2058·139 (5)	48571·95	$3p\,^1D_2-5s\,^1P_1$
2054·85 (1)	48652·31	
2011·05 (0)	49709·20	
2008·55 (00)	49771·05	
λ_{vac} (Int.).		
1991·94 (2)	50202·3	$3p\,^1D_2-3d\,^3P$
1989·01 (6)	50276·4	$3p\,^3P_2-3p'\,^3P_2$
1986·39 (4)	50342·6	$P_2 \quad P_1$
1984·50 (0)	50390·5	
1983·25 (4)	50422·3	$P_1 \quad P_2$
1980·64 (3)	50488·7	$P_1 \quad P_1$
1979·23 (3)	50524·7	$P_1 \quad P_0$
1977·62 (3)	50565·8	$P_0 \quad P_1$
1963·04 (00)	50941·4	
1962·13 (0)	50965·0	
1961·29 (00)	50986·8	
1960·16 (0)	51016·2	
1958·65 (0)	51055·6	
1957·92 (0)	51074·6	
1956·06 (0)	51123·2	
1955·00 (1)	51150·9	Si ?
1953·02 (0)	51202·8	
1952·53 (00)	51215·6	
1951·61 (0)	51239·7	
1950·23 (0)	51276·0	
1947·01 (1)	51360·8	
1945·03 (00)	51413·1	
1942·37 (00)	51483·5	
1940·69 (0)	51528·1	
1934·49 (00)	51693·2	

† McLennan and Shaver.
‡ Not in previous list.
§ Solar wave-lengths adopted between these limits.
* Calculated wave-lengths adopted.

Table I—(continued).

λ_{vac} (Int.).	ν.	Classification.
*1904·643 (2)	52503·29	$3p\,^1D_2-4d\,^1P_1$
1901·36 (8R)	52593·9	$3p\,^1D_2-4d\,^1F_3$
1893·25 (5)	52819·2	$3p\,^1D_2-4d\,^1D_2$
1887·74 (2)	52973·4	$3p\,^1D_2-6s\,^3P_1$
1883·80 (0)	53084·2	
*1881·883 (2)	53138·25	$3p\,^3P_2-3d\,^1F_3$
*1880·988 (0)	53163·53	$3p\,^3P_2-3d\,^1P_1$
*1875·835 (2)	53309·61	$3p\,^3P_1-3d\,^1P_1$
1874·90 (3)	53336·2	$3p\,^1D_2-6s\,^1P_1$
*1873·127 (2)	53386·67	$3p\,^3P_0-3d\,^1P_1$
1865·19 (0)	53613·8	
1861·76 (00)	53712·6	$3p\,^1D_2-4d\,^3P$?
1855·62 (00)	53890·3	
1853·17 (1)	53961·6	$3p\,^3P_2-3d\,^3D_1$
1852·49 (3)	53981·4	$3p\,^3P_2-3d\,^3D_2$
1851·82 (1)	54000·9	
1850·70 (5R)	54033·6	$3p\,^3P_2-3d\,^3D_3$
*1848·768 (2)	54090·11	$3p\,^3P_2-5s\,^3P_1$
1848·17 (3)	54107·6	$3p\,^3P_1-3d\,^3D_1$
1847·48 (4R)	54127·8	$3p\,^3P_1-3d\,^3D_2$
1846·13 (2)	54167·4	$3p\,^3P_1-5s\,^3P_0$
1845·53 (3)	54185·0	$3p\,^3P_0-3d\,^3D_1$
*1843·788 (2)	54236·19	$3p\,^3P_1-5s\,^3P_1$
1841·48 (3)	54304·2	$3p\,^3P_2-5s\,^3P_2$
*1841·171 (2)	54313·25	$3p\,^3P_0-5s\,^3P_1$
1838·00 (1)	54407·0	
1836·54 (2)	54450·2	$3p\,^3P_1-5s\,^3P_2$
*1829·910 (2)	54647·48	$3p\,^3P_2-5s\,^1P_1$
1826·45 (00)	54751·0	
*1825·032 (00)	54793·56	$3p\,^3P_1-5s\,^1P_1$
*1822·469 (2)	54870·62	$3p\,^3P_0-5s\,^1P_1$
1817·97 (0)	55006·4	$3p\,^1D_2-5d\,^1P_1$?
1814·07 (6)	55124·7	$3p\,^1D_2-5d\,^1F_3$
1809·05 (4)	55277·6	$3p\,^1D_2-5d\,^1D_2$
1799·16 (2)	55581·5	$3p\,^1D_2-7s\,^1P_1$
1797·35 (1)	55637·5	$3p\,^1D_2-5d\,^3P$?
1790·31 (2)	55856·3	
1787·78 (00)	55935·3	
1784·09 (0)	56051·0	
1783·24 (2*n*)	56077·7	
1776·86 (2)	56279·0	$3p\,^3P_2-3d\,^3P$?
1774·98 (0)	56338·7	
1774·05 (00)	56368·2	
1772·26 (0)	56425·1	$3p\,^3P_1-3d\,^3P$?
1770·89 (3R)	56468·8	$3p\,^1D_2-6d\,^1F_3$
1769·81 (3)	56503·2	$3p\,^3P_0-3d\,^3P$? $3p\,^1D_2-x_1$
1766·09 (4*n*)	56622·3	
1765·15 (3R)	56652·4	$3p\,^1D_2-6d\,^1D_2$
1759·63 (2)	56830·1	$3p\,^1D_2-8s\,^1P_1$
1757·34 (00)	56904·2	
1753·11 (3*n*)	57041·5	
1752·71 (0)	57054·5	
1749·78 (00)	57150·0	
1747·40 (1)	57227·9	
1743·91 (0)	57342·4	
1740·40 (2*n*)	57458·1	$3p\,^1D_2-7d\,^1D_2$
1736·58 (00)	57584·7	$3p\,^1D_2-9s\,^1P_1$
1734·78 (1*n*)	57644·2	
1727·37 (00)	57891·5	
1724·07 (00)	58002·3	
*1707·102 (0)	58578·82	$3p\,^3P_2-4d\,^1P_1$
1704·47 (3R)	58669·3	$3p\,^3P_2-4d\,^1F_3$
*1702·855 (2)	58724·90	$3p\,^3P_1-4d\,^1P_1$
*1700·623 (2)	58801·96	$3p\,^3P_0-4d\,^1P_1$
1700·43 (2)	58808·6	$3p\,^3P_2-4d\,^3D_2$
1699·73 (00)	58832·9	
1698·25 (00)	58884·1	
1697·92 (4R)	58895·6	$3p\,^3P_2-4d\,^3D_3$
1697·60 (0)	58906·7	
1696·22 (3R)	58954·6	$3p\,^3P_1-4d\,^3D_2$
1695·60 (2)	58976·2	$3p\,^3P_0-4d\,^3D_1$
1693·48 (1)	59050·0	$3p\,^3P_2-6s\,^3P_1$
1693·23 (1)	59058·7	
1690·80 (1)	59143·6	$3p\,^3P_1-6s\,^3P_0$
1689·30 (1)	59196·1	$3p\,^3P_1-6s\,^3P_1$
1687·08 (0)	59274·0	$3p\,^3P_0-6s\,^3P_1$
1686·87 (1)	59281·4	$3p\,^3P_2-6s\,^3P_2$
1682·70 (1)	59428·3	$3p\,^3P_1-6s\,^3P_2$
1676·83 (0)	59636·3	
1675·24 (3)	59692·9	
1672·62 (2)	59786·4	$3p\,^3P_2-4d\,^3P$
1670·91 (2)	59847·6	
1668·53 (1)	59933·0	$3p\,^3P_1-4d\,^3P$
1667·66 (1)	59964·3	
1666·40 (1)	60009·6	$3p\,^3P_0-4d\,^3P$
1664·51 (1)	60077·7	
1660·44 (0)	60225·0	
1653·28 (1)	60485·8	
1651·02 (0)	60568·6	
1633·95 (1*n*)	61201·4	$3p\,^3P_2-5d\,^1F_3$
1633·04 (0*n*)	61235·5	
1631·39 (0*n*)	61297·4	
1629·33 (1)	61374·9	
1627·83 (00)	61431·5	
1627·15 (00)	61457·1	
1625·68 (2*n*)	61512·7	Si ?
1622·79 (2*n*)	61622·3	Si ?
1620·39 (1)	61713·5	$3p\,^3P_2-5d\,^3P$?
1616·55 (1)	61860·1	$3p\,^3P_1-5d\,^3P$?
1615·94 (1)	61883·5	
1614·63 (1)	61933·7	$3p\,^3P_0-5d\,^3P$?
1609·02 (0)	62149·6	
1605·86 (0)	62271·9	
1597·99 (1)	62579·6	$3p\,^3P_2-x_1$
1595·21 (0)	62687·7	
1594·25 (1)	62725·4	$3p\,^3P_1-x_1$ $3p\,^3P_2-6d\,^1D_2$
1592·27 (1)	62803·4	$3p\,^3P_0-x_1$
1590·60 (0)	62869·4	$3p\,^3P_1-6d\,^1D_2$

* Calculated wave-lengths adopted.

air, and those smaller than λ 2000 *in vacuo*. The second column gives the corresponding wave-numbers, reduced to vacuum throughout, while the third indicates the classification of the lines, the justification for which will appear later.

Table IA.—Other Lines which appear in the Photographs.

λ_{vac} (Int.).	Probable origin.	λ_{vac} (Int.).	Probable origin.
2073·37 (1)	Si II	1769·20 (00)	Al
2072·68 (0)		1763·93 (1)	Al II
2026·49 (1)	Mg I	1762·95 (0)	Al I ?
1936·45 (2*n*)	Al I ?	1745·26	N I
1932·25 (2*n*)		1742·74	
1862·41 (00)	Al II	1725·00 (00)	Al II
1840·09 (0)	Ca II*	1721·30 (00)	
1816·98 (2)	Si II	1670·78 (2)	Al II
1808·09 (1)			

* The other component of the Ca pair is masked by Si 1838·00.

The first three lines in Table I are the strongest of those photographed in the near infra-red by McLennan and Shaver.* Following these are 14 lines for which the new solar wave-lengths on the International scale have been adopted†; these are slightly different from the values given in the previous table, and λ 5754·240 has been added to the original list. No change has been found necessary from λ 3020 to λ 2208, except that three faint lines have been added. From the next line at λ 2124 to λ 1841, however, new wave-lengths have been substituted for those previously published, and several faint lines which are believed to be due to silicon have been included. Many of the lines of shorter wave-length than λ 1841 appear to have been observed in the vacuum arc by McLennan and Shaver, but only approximate wave-lengths were given by these observers.

Lines which appear in the photographs but have not been included in the general table are indicated in Table IA; it is possible that some of these may obscure lines of silicon. Lines for which wave-lengths have been calculated in the manner already explained are marked with an asterisk.

Predicted Terms.

The terms corresponding with the various electron configurations of Si I are indicated in Table II. The notation is similar to that adopted in previous

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* 'Trans. Roy. Soc. Canada,' vol. 18, p. 21 (1924).

† Revision of "Rowland's Preliminary Table of Solar Spectrum Wave-lengths," by C. E. St. John and others, Carnegie Institution, 1928.

Table II.—Predicted Terms of Si I.

1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	6_1	Effective configuration.	Term prefix.	Terms.
2	2	6	2	2									$s^2 p^2$	$3p$	$^3\mathbf{P}$ $^1\mathbf{D}$ $^1\mathrm{S}$
2	2	6	2	1		1							$s^2 p . s$	$4s$	$^3\mathbf{P}$ $^1\mathbf{P}$
2	2	6	1	3									$s p^3$	$3p'$	$^5\mathrm{S}$ $^3\mathbf{D}$ $^3\mathbf{P}$ $^3\mathrm{S}$ $^1\mathbf{D}$ $^1\mathrm{P}$
2	2	6	2	1			1						$s^2 p . p$	*$4p$	$^3\mathrm{D}$ $^3\mathrm{P}$ $^3\mathrm{S}$ $^1\mathbf{D}$ $^1\mathrm{P}$ $^1\mathbf{S}$
2	2	6	2	1	1								$s^2 p . d$	$3d$	$^3\mathrm{F}$ $^3\mathbf{D}$ $^3\mathbf{P}$ $^1\mathbf{F}$ $^1\mathrm{D}$ $^1\mathbf{P}$
2	2	6	2	1		1							$s^2 p . s$	$5s$	$^3\mathbf{P}$ $^1\mathbf{P}$
2	2	6	2	1			1						$s^2 p . p$	$5p$	$^3\mathbf{D}$ $^3\mathbf{P}$ $^3\mathrm{S}$ $^1\mathbf{D}$ $^1\mathrm{P}$ $^1\mathbf{S}$
2	2	6	2	1				1					$s^2 p . d$	$4d$	$^3\mathrm{F}$ $^3\mathbf{D}$ $^3\mathbf{P}$ $^1\mathbf{F}$ $^1\mathrm{D}$ $^1\mathbf{P}$
2	2	6	2	1					1				$s^2 p . f$	$4f$	$^3\mathrm{G}$ $^3\mathrm{F}$ $^3\mathbf{D}$ $^1\mathrm{G}$ $^1\mathrm{F}$ $^1\mathrm{D}$

* The principal combinations of this row of terms are outside the range of the observations, in the infra-red.

papers,† terms in each row being prefixed by the n_k designation of the wandering electron; in the special case of the configuration sp^3, the adopted prefix is $3p'$. Combinations between terms on different rows, other than $3p'$, are governed by the condition $\Delta k = \pm 1$ ($k = 1, 2, 3, \ldots$ for $s, p, d, \ldots$), and by the rule for inner quantum numbers associated with the term symbols, namely $\Delta j = \pm 1$ or 0, with $0 \rightarrow 0$ forbidden. Combinations of the p' terms with the others follow the rule $\Delta k = 0$, so that of the terms shown in the table only the p terms can combine with the p' terms, always subject to the inner quantum rules. These conditions are equivalent to the rule for permissible electron transitions; namely, that $\Delta k = \pm 1$ for one electron, and $\Delta k = 0$ or 2 for a second electron when two transitions occur together.

Identification of Terms.

The terms which are believed to have been identified are indicated by heavier type in Table II. They are shown, with the observed combinations, in Tables III and IIIA. There can be little doubt as to most of these, but some of the assignments presented considerable difficulty in the first instance. In particular, it should be noted that the $3p'$ and $3d$ terms yield similar combinations with the deep $3p$ terms, so that the $3p'$ terms might have been called $3d$, and subsequent d terms $4d$ and $5d$. In support of the assignments adopted, however, the first $^3\mathrm{D}$ term does not appear to be in reasonable sequence with the second and third, and it has accordingly been identified as $3p'\,{}^3\mathrm{D}$. Again, the terms designated by $3p'\,{}^3\mathrm{P}$ and $3p'\,{}^1\mathrm{D}_2$ do not appear to be followed by other terms related to them in Rydberg sequences, as would be expected if they

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† 'Roy. Soc. Proc.,' A, vol. 117, p. 317 (1928); vol. 118, p. 34 (1928).

Table III.—Combinations in Si I.

Terms.		$\Delta\nu$	$3p\ ^3P_0$ 65765·00	$3p\ ^3P_1$ 65687·94	$3p\ ^3P_2$ 65541·86	$3p\ ^1D_2$ 59466·33	$3p\ ^1S_0$ 50370·90
			77·06	*146·08*	*6075·53*	*9095·43*	
$4s\ ^3P_0$	26082·05			39605·89 (9)			
		77·14					
P_1	26004·91		39760·04 (7)	39683·03 (8)	39537·01 (10)	33461·39 (5)	24365·89 (5)
		194·79					
P_2	25810·12			39877·83 (10)	39731·73 (15)	33656·27 (2)	
$4s\ ^1P_1$	24773·40		40991·64 (3)	40914·54 (3)	40768·42 (3)	34692·97 (10)	25597·61 (10)
$3p'\ ^3D_1$	20488·94		45276·09 (2)	45198·92 (2)	45052·96 (1)		
		17·05					
D_2	20471·89			45216·07 (3)	45069·96 (2)		
		28·35					
D_3	20443·54				45098·32 (4)		
$3p'\ ^1D_2$	18413·72			*47274·22 (0)	*47128·14 (1)	41052·61 (8)	
$3p'\ ^3P_2$	15265·5			50422·3 (4)	50276·4 (6)		
		— 66·3					
P_1	15199·2		50565·8 (3)	50488·7 (3)	50342·6 (4)		
		—36·0					
P_0	15163·2			50524·7 (3)			
$3d\ ^1F_3$	12403·61				*53138·3 (2)	47062·72 (10)	
$3d\ ^1P_1$	12378·33		*53386·7 (2)	*53309·6 (2)	*53163·5 (0)	*47088·00 (2)	37992·57 (5)
$3d\ ^3D_1$	11580·2		54185·0 (3)	54107·6 (3)	53961·6 (1)		
		19·9					
D_2	11560·3			54127·8 (4)	53981·4 (3)		
		52·0					
D_3	11508·3				54033·6 (5)		
$3d\ ^1D_2$	11506·2					47960·09 (2)	
$5s\ ^3P_0$	11520·5			54167·4 (2)			
		68·8					
P_1	11451·7		*54313·3 (2)	*54236·2 (2)	*54090·1 (2)	*48014·58 (1)	38919·15 (2)
		214·0					
P_2	11237·7			54450·2 (2)	54304·2 (3)		
$5s\ ^1P_1$	10894·4		*54870·6 (2)	*54793·6 (00)	54647·5 (2)	*48571·95 (5)	39476·52 (2)
? $3d\ ^3P$	9262·8		†	56425·1 (0)	56279·0 (2)	50202·3 (2)	

* Calculated values. † Masked by 56503 (3).

Table III—(continued).

	Terms.	$\Delta\nu$	$3p\ ^3P_0$ 65765·00	$3p\ ^3P_1$ 65687·94	$3p\ ^3P_2$ 65541·86	$3p\ ^1D_2$ 59466·33	$3p\ ^1S_0$ 50370·90
			77·06	146·08	6075·53	9095·43	
$4d\ ^1P_1$	6963·0		*58802·0 (2)	*58724·9 (2)	*58578·8 (0)	*52503·3 (2)	43407·9 (2)
$4d\ ^1F_3$	6872·5				58669·3 (3)	52593·9 (8)	
$4d\ ^3D_1$	6788·8	55·5	58976·2 (2)	†[58899·1]	[58753·0]		
D_2	6733·3	87·0		58954·6 (3)	58808·6 (2)		
D_3	6646·3				58895·6 (4)		
$4d\ ^1D_2$	6647·1					52819·2 (5)	
$6s\ ^3P_0$	6544·3	52·7		59143·6 (1)			
P_1	6491·6	231·5	59274·0 (0)	59196·1 (1)	59050·0 (1)	52973·4 (2)	43880·4 (0)
P_2	6260·1			59428·3 (1)	59281·4 (1)		
$6s\ ^1P_1$	6129·3					53336·2 (3)	44242·5 (1)
$4d\ ^3P$?	5755·3		60009·6 (1)	59933·0 (1)	59786·4 (2)	53712·6 (00)	
$5d\ ^1P_1$?	4459·9					55006·4 (0)	
$5d\ ^1F_3$	4341·6				61201·4 (1)	55124·7 (6)	
$5d\ ^1D_2$	4189					55277·6 (4)	
$7s\ ^1P_1$	3885					55581·5 (2)	
$5d\ ^3P$?	3829		61934 (1)	61860 (1)	61714 (1)	55637 (1)	
$6d\ ^1F_3$	2997					56469 (3)	
x_1	2963		62803 (1)	62725 (1)	62580 (1)	56503 (3)	
$6d\ ^1D_2$	2817			62869 (0)	62725 (1)	56652 (3)	
$8s\ ^1P_1$	2636					56830 (2)	
$7d\ ^1D_2$	2008					57458 (2)	
$9s\ ^1P_1$	1881					57585 (00)	

* Calculated values. † Masked by 58895·6 (4).

Table IIIA.—Less Refrangible Combinations in Si I.

Terms.	$\Delta\nu$	$4s\ {}^3P_0$ 26082·05		$4s\ {}^3P_1$ 26004·91		$4s\ {}^3P_2$ 25810·12	$4s\ {}^1P_1$ 24773·40	$3d\ {}^1F_3$ 12403·61
			77·14		*194·79*			
$4p\ {}^1D_2$? 22652								10248 (10)
$4p\ {}^1S_0$ 15873				10131 (5)			8902 (8)	
$5p\ {}^3D_1$ 8762·28		17319·77 (1)						
	14·56							
D_2 8747·72				17257·19 (2)				
	180·54							
D_3 8567·18						17242·94 (3)		
$5p\ {}^3P_0$ 8469·33				17535·58 (1)				
	32·90							
P_1 8436·43		17645·61 (1)		17568·49 (2)		17373·68 (0)		
	139·47							
P_2 8296·96				17707·94 (1)		17513·17 (5)		
$5p\ {}^1S_0$ 7967·23							16806·17 (5)	

were $3d\ {}^3P$ and $3d\ {}^1D_2$. There appears also to be a definite range of higher term values associated with $3p'$ as compared with those distinguished by $3d$; with the identifications adopted, the deepest $3d$ terms range about 12000, as in many other spectra. The assignment of the $3p'$ terms is also supported by comparisons with the P II spectrum, as will appear later.

The arrangement of the deeper terms in Table III is similar to that given empirically by McLennan and Shaver,* and afterwards interpreted in relation to electronic configurations by Hund.† More precise values of the terms have now been determined, and numerous additional terms have been identified. Many of the new terms are established by confirmatory combinations, but the identification of some of them depends upon extrapolation from preceding terms. The more doubtful identifications are indicated by a ? mark.

The triplet series $3p\ {}^3P - ms\ {}^3P$, of which three members have been completely observed, is fully established by combinations, and may be used with confidence for the determination of term values. Of the series $3p\ {}^3P - md\ {}^3D$, however, only two members have been identified. The $3p\ {}^3P - md\ {}^3P$ is either feeble or missing, and the partial identifications shown in the table are possibly somewhat doubtful; there is evidence from P II and S III, however, that the $d\,^3P$ separations may be so small in Si I as to be unresolvable in the present series of photographs.

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* *Loc. cit.*

† 'Zeit. f. Phys.,' vol. 33, p. 335 (1925).

Term Values.

Several series of more than two members are available for the determination of term values. It will be of interest first to consider the series $3p\,^3P - ms\,^3P$. Using the Hicks' formula with the lines indicated below, and observing from Table III that $3p\,^3P_0 - 3p\,^3P_1 = 77{\cdot}1$, $3p\,^3P_0 - 3p\,^1D_2 = 6298{\cdot}7$, the term values shown are readily obtained.

$$\left.\begin{array}{r} 3p\,^3P_1 - 4s\,^3P_0 = 39606 \\ - 5s\,^3P_0 = 54167 \\ - 6s\,^3P_0 = 59144 \end{array}\right\} \begin{array}{l} \nu = 65668 - R/[m + 1{\cdot}12594 - 0{\cdot}07397/m]^2 \\ 3p\,^3P_0 = 65745;\ 3p\,^1D_2 = 59446. \end{array}$$

$$\left.\begin{array}{r} 3p\,^3P_1 - 4s\,^3P_1 = 39683 \\ - 5s\,^3P_1 = 54236 \\ - 6s\,^3P_1 = 59196 \end{array}\right\} \begin{array}{l} \nu = 65702 - R/[m + 1{\cdot}13359 - 0{\cdot}07991/m]^2 \\ 3p\,^3P_0 = 65779;\ 3p\,^1D_2 = 59480. \end{array}$$

$$\left.\begin{array}{r} 3p\,^3P_1 - 4s\,^3P_2 = 39878 \\ - 5s\,^3P_2 = 54450 \\ - 6s\,^3P_2 = 59428 \end{array}\right\} \begin{array}{l} \nu = 65952 - R/[m + 1{\cdot}12617 - 0{\cdot}07469]^2 \\ 3p\,^3P_0 = 66029;\ 3p\,^1D_2 = 59730. \end{array}$$

Other series taken from the same multiplets necessarily give the same values for the components of $3p\,^3P$ when corresponding components of $s\,^3P$ are taken for calculation.

It will be seen that $s\,^3P_0$ and $s\,^3P_1$ give approximately the same limits, whilst $s\,^3P_2$ leads to a considerably greater value. This was to be expected from Hund's theory, according to which, in the present spectrum, $s\,^3P_0$ and $s\,^3P_1$ tend towards the limit $^2P_1$ of Si II and $s\,^3P_2$ towards the limit $^2P_2$. These limits differ by 287 units of wave-number,* and the mean of the above values from $s\,^3P_0$ and $s\,^3P_1$ is actually smaller than that from $s\,^3P_2$ by 267 units. The agreement is as close as can be expected, in view of the inadequacy of the series formula and the possible errors of wave-numbers in the Schumann region.

If the mean value (65762) be adopted for $3p\,^3P_0$, all other sets of corresponding terms which tend to the limit $^2P_1$ will form Rydberg sequences. For those tending to the limit $^2P_2$, however, the values directly determined from the combinations, as they appear in Table III, will only form Rydberg sequences when they have been increased by 287. In other words, for terms which tend to the ${}^2\mathrm{P}_2$ limit, the values determined from formulæ must be diminished by 287 units in order to refer them to the lowest level $3p\,{}^3\mathrm{P}_0$.

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* A. Fowler, 'Phil. Trans.,' A, vol. 225, p. 24 (1925).

According to Hund, all the singlet series of Si I should tend towards the limit ${}^2\mathrm{P}_2$ of Si II. This is apparently true of the series $3p\,{}^1\mathrm{D}_2 - ms\,{}^1\mathrm{P}_1$, for which the data and a Hicks' formula are given below :—

$$\begin{array}{ll}
3p\,{}^1\mathrm{D}_2 - 4s\,{}^1\mathrm{P}_1 = 34693\ (10) & \\
\left.\begin{array}{r} -\,5s\,{}^1\mathrm{P}_1 = 48572\ (5) \\ -\,6s\,{}^1\mathrm{P}_1 = 53336\ (3) \\ -\,7s\,{}^1\mathrm{P}_1 = 55581\ (2) \end{array}\right\} & \begin{array}{l} \nu = 59714 - \mathrm{R}/[m + 1\cdot16731 - 0\cdot05803/m]^2 \\ 3p\,{}^1\mathrm{D}_2 = 59714\,;\ 3p\,{}^3\mathrm{P}_0 = 66013. \end{array} \\
\qquad\qquad -\,8s\,{}^1\mathrm{P}_1 = 56830\ (1) & \\
\qquad\qquad -\,9s\,{}^1\mathrm{P}_1 = 57585\ (00) &
\end{array}$$

Extrapolation to the first line gives O — C = — 356, and to the last + 12 and + 13 units of wave-number respectively. If the identification of the last two lines be correct, as seems probable, the term values above deduced are rather too small, but it is sufficiently clear that the series under consideration tends to the same limit (${}^2\mathrm{P}_2$) as the $s\,{}^3\mathrm{P}_2$ terms.

The remaining singlet series present considerable difficulty. The strongest of them is $3p\,{}^1\mathrm{D}_2 - md\,{}^1\mathrm{F}_3$, for which the data are as follows :—

$$\begin{array}{ll}
\left.\begin{array}{r} 3p\,{}^1\mathrm{D}_2 - 3d\,{}^1\mathrm{F}_3 = 47063\ (8) \\ -\,4d\,{}^1\mathrm{F}_3 = 52594\ (8) \\ -\,5d\,{}^1\mathrm{F}_3 = 55125\ (6) \end{array}\right\} & \begin{array}{l} \nu = 59572 - \mathrm{R}/[m + 0\cdot97325 - 0\cdot02281/m]^2 \\ 3p\,{}^1\mathrm{D}_2 = 59572\,;\ 3p\,{}^3\mathrm{P}_0 = 65871. \end{array} \\
\qquad\qquad -\,6d\,{}^1\mathrm{F}_3 = 56469\ (3) &
\end{array}$$

The choice of the last line appears to be justified by the fact that the formula gives the wave-number as 56492, and by its appearance with undiminished intensity in potassium fluo-silicate, as in the case of the preceding members of this series. The inclusion of this line, however, modifies the calculated limit of the series very considerably. Thus, the last three lines give the formula

$$\nu = 59482 - \mathrm{R}/[m + 1\cdot100325 - 0\cdot326836/m]^2$$

from which the calculated value of the first line is 46759 (O — C = + 306). If all four lines are included in a formula with a second correcting term, β/m^2, the limit becomes 59453. This is nearly the mean of the two values deduced from $3p\,{}^3\mathrm{P}_1 - ms\,{}^3\mathrm{P}_{01}$, and it seems probable that, in opposition to Hund's theory, the singlet DF series tends to the limit ${}^2\mathrm{P}_1$ of Si II. Other discordances with the theory of limits have been found by Shenstone* and by Lang and Laporte.†

The singlet $3p\,{}^1D_2 - md\,{}^1D_2$ series appears to consist of the lines shown below :—

$$3p\,{}^1D_2 - 3d\,{}^1D_2 = 47964\ (2)$$

$$\left.\begin{array}{l} - 4d\,{}^1D_2 = 52819\ (5) - \\ - 5d\,{}^1D_2 = 55278\ (4) - \\ - 6d\,{}^1D_2 = 56652\ (3) \\ - 7d\,{}^1D_2 = 57458\ (2) - \end{array}\right\} \begin{array}{l} \nu = 59737 - R/[m + 0\cdot89538 + \\ \qquad\qquad\qquad 0\cdot26220/m]^2 \\ 3p\,{}^1D_2 = 59737\ ;\ 3p\,{}^3P_0 = 66036. \end{array}$$

The formula has been calculated from the second, third and fifth lines. The first line, if correctly identified, is abnormally weak as compared with succeeding members of the series, but it appears to be the only observed line available. The second and third lines, as will appear from Table III, are remarkable as giving $d\,{}^1D_2$ terms which are practically identical with $d\,{}^3D_3$ terms; they appear, however, to be too strong to be regarded as $3p\,{}^1D_2 - 3d$, $4d\,{}^3D_3$, especially as $3p\,{}^1D_2 - 3d$, $4d\,{}^3D_2$, which would be expected to be still stronger lines, are missing. The fourth line has been chosen in preference to 56622 because, like the second and third, it is much weakened in potassium fluo-silicate, while 56622 is scarcely affected, as compared with its appearance in elementary silicon. The selection of 56652 is also supported by the apparent combinations of $6d\,{}^1D_2$ with $3p\,{}^3P_{21}$. The series, however, is not very closely represented by a Hicks' formula ; by extrapolation with the formula given above, the wave-number of the first line appears as 47757 (O − C = + 207), while the computed value for the fourth is 56635 (O − C = + 17). A formula calculated from the second, third and fourth lines gives $3p\,{}^1D_2 = 59805$; and if 56622 be substituted for 56652, $3p\,{}^1D_2 = 59686$. Thus, while the series is not well represented by formulæ, it is reasonable to conclude that it leads to a value for $3p\,{}^3P_0$ similar to that deduced from $3p\,{}^3P_2 - ms\,{}^3P_2$, and that the $d\,{}^1D_2$ series tends to the limit ${}^2P_2$ of Si II, in agreement with theory.

The series $3p\,{}^1D_2 - md\,{}^1P_1$ is very feebly represented. The identification of the first two members is strongly supported by combinations, but the choice of the third depends upon extrapolation from the first two, and the order of occurrence of adjacent terms. Details of the series are as follows :—

$$\left.\begin{array}{l} 3p\,{}^1D_2 - 3d\,{}^1P_1 = 47088\ (2) \\ \qquad\ \ - 4d\,{}^1P_1 = 52503\ (2) \\ \qquad\ \ - 5d\,{}^1P_1 = 55006\ (0) \end{array}\right\} \begin{array}{l} \nu = 59436 - R/[m + 0\cdot97305 + \\ \qquad\qquad\qquad 0\cdot01617/m]^2 \\ 3p\,{}^1D_2 = 59436\ ;\ 3p\,{}^3P_0 = 65735. \end{array}$$

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* 'Phys. Rev.,' vol. 31, p. 317 (1928).

† 'Phys. Rev.,' vol. 31, p. 763 (1928).

The value of $3p\,^3P_0$ thus determined suggests that the $d\,^1P_1$ series tends to the $^2P_1$ limit of Si II, in opposition to theory, but the evidence for this is not very conclusive, in consequence of the few observed members of the series.

If the identifications of the near infra-red singlets shown in Table IIIA be correct, another series of three terms becomes available for the calculation of term values, namely,

$$\left.\begin{array}{rr} 4s\,^1P_1 - 3p\,^1S_0 = & -25598 \\ - 4p\,^1S_0 = & 8902 \\ - 5p\,^1S_0 = & 16806 \end{array}\right\} \begin{array}{l} \nu = 25022 - R/[m + 0\cdot74580 - \\ \qquad\qquad\qquad\qquad 0\cdot27340/m]^2 \\ 3p\,^3P_0 = 66014;\ 3p\,^1D_2 = 59715. \end{array}$$

The close agreement of the value for $3p\,^3P_0$ thus determined with that derived from the series $3p\,^3P_1 - ms\,^3P_2$ not only indicates that the $p\,^1S_0$ series tends to the limit $^2P_2$ of Si II, as expected, but strongly supports the identification of the two less refrangible singlets which are involved.

As a result of the foregoing considerations, the term $3p\,^3P_0$, representing the lowest normal state of the Si I atom, has been assigned the value 65765. All the other terms shown in Tables III and IIIA are accordingly based upon this, and represent the energy levels as reckoned from $^2P_1$ of Si II. All the series of terms tending to $^2P_1$ may thus be represented by series formulæ without modification. Those which tend to the $^2P_2$ limit, however, must be increased by 287 units in order that they may form Rydberg sequences.

The general consistency of the scheme of terms will appear from Table IV (p. 436), which shows the effective quantum numbers, or Rydberg denominators, for the various terms, R being taken as 109737.

The ionisation potential of Si I represented by the adopted value of $3p\,^3P_0$ is 8·12 volts.

Intensities.

The intensities of some of the lines show marked irregularities. Thus, the first line of the triplet $3p\,^3P - 3d\,^1P_1$ at ν 53163 is of intensity 0, while the other two members, which would be expected to be weaker, are of intensity 2. A similar irregularity is found also in the next triplet of this series, having its first line at ν 58578. Again, in the triplet $3p\,^3P - 5s\,^1P_1$, the middle line at ν 54793 is very much fainter than the outer members of the triplet.

It is possible that the intensities of some of the lines, as observed in the arc by the method adopted for silicon, are affected by absorption due to atmospheric gases and to products of combustion. One of the photographs of potassium fluo-silicate was remarkable as showing very strong absorption bands of nitric

Table IV.—Rydberg Denominators.

	$^3P_0$.*	$^3P_1$.*	$^3P_2$.	$^1P_1$.
4*s*	2·0512	2·0542	2·0506	2·0926
5*s*	3·0863	3·0956	3·0858	3·1328
6*s*	4·0949	4·1115	4·0940	4·1356
7*s*				5·1287
8*s*				6·1272
9*s*				7·1145

	$^1F_3$.*	$^1P_1$.*	$^3D_1$.*	$^3D_2$.*	$^3D_3$.	$^1D_2$.	^3P ?.
3*d*	2·9744	2·9774	3·0784	3·0810	3·0502	3·0508	3·4421
4*d*	3·9959	3·9699	4·0204	4·0371	3·9785	3·9782	4·3667
5*d*	5·0275	4·9603 ?				4·9514	5·3542
6*d*	5·0506					5·9487	
7*d*						6·9149	

	$^3P_0$.*	$^3P_1$.*	$^3P_2$.	$^1D_2$.	$^1S_0$.
3*p*	1·2917	1·2925	1·2911	1·3552	1·4718
4*p*	—	—	—	2·1872 ?	2·6056
5*p*	3·5996	3·6066	3·5755		3·6462

* The values in these columns have been computed from the corresponding terms shown in Table III; for the remaining terms the values indicated in Table III have been increased by 287 units for the calculation of n^*.

oxide,[†] which totally obliterated many of the lines of silicon. This suggests that given small amounts of nitric oxide produced by the arc may be effective in reducing the intensities of some of the lines, and it is possible that the low intensity of ν 53163 may be accounted for in this way. The spectrum of nitric oxide is under investigation, in order to determine its possible effects on other lines.

Nitrogen itself produces absorption bands, but the strongest of them lie outside the range of the present observations, on the more refrangible side.

Comparison with P II.

The elements of successively higher atomic numbers than silicon are phosphorus, sulphur and chlorine, so that Si I, P II, S III and Cl IV form an iso-electronic series. The triplets of P II have been investigated in considerable detail by Bowen,[‡] but no account has been given of the singlets of this spectrum. A few of the higher triplet combinations of S III have been identified by M. J. Gilles,[†] and a few of the deeper combinations of Cl IV by Bowen,[‡] but in neither case has any determination of term values yet become possible. Effective comparison can accordingly at present be made only between the triplets of Si I and P II.

[†] See Leifson, 'Astrophys. Jour.,' vol. 63, p. 82 (1926).

[‡] 'Phys. Rev.,' vol. 29, p. 510 (1927); see also a note on P II and Si I in a paper on Cl IV, 'Phys. Rev.,' vol. 31, p. 36 (1928).

The terms and triplet separations in the two spectra are shown side by side in Table V, and the values of the P II terms, as given by Bowen, are also

Table V.—Terms of Si I compared with those of P II.

	Si I.		P II.			$\Delta\nu$: P II/Si I.
	ν.	$\Delta\nu$.	ν.	$\Delta\nu$.	$\nu/4$.	
$3p\ ^3P_0$	65765·00		160497·7		40124·4	
		77·06		*165·3*		
P_1	65687·94		160332·4		40083·1	2·16
		146·08		*304·6*		
P_2	65541·86		160027·8		40007·0	
$4s\ ^3P_0$	26082·05		73900·0		18475·0	
		77·14		*146·4*		
P_1	26004·91		73753·6		18438·4	1·94
		194·79		*380·7*		
P_2	25810·12		73372·9		18343·2	
$3p'\ ^3D_1$	20488·94		95246·0		23811·5	
		17·05		*20·3*		
D_2	20471·89		95225·7		23806·4	1·21
		28·35		*34·7*		
D_3	20443·54		95191·0		23797·8	
$3p'\ ^3P_2$	15265·5		83733·9		20918·7	
		−66·3		*−48·4*		
P_1	15199·2		83685·5		20921·4	0·59
		−36·0		*−11·8*		
P_0	15163·2		83674·7		20933·5	
$^*4p\ ^3D_1$			57332·0		14333·0	
				173·5		
D_2			57158·5		14289·6	
				328·7		
D_3			56829·8		14207·5	
$^*4p\ ^3P_0$			55273·2		13818·3	
				78·1		
P_1			55195·1		13798·8	
				247·3		
P_2			54947·8		13737·0	

* The principal combinations of these terms in Si I are out of range in the infra-red.

[†] 'C. R.,' vol. 188, p. 63 (1929).

[‡] 'Phys. Rev.,' vol. 31, p. 34 (1928).

Table V—(continued).

	Si I.		P II.			$\Delta\nu$: P II/Si I.
	ν.	$\Delta\nu$.	ν.	$\Delta\nu$.	$\nu/4$	
$3d\ {}^3D_1$	11580·2		56443·1		14110·8	
		19·9		*48·4*		
D_2	11560·3		56394·7		14098·7	1·97
		52·0		*93·4*		
D_3	11508·3		56301·3		14075·3	
$3d\ {}^3P_0$			—		—	
				—		
P_1	9262 ?		50243·8		12561·0	
				38·6		
P_2			50205·2		12551·3	
$5s\ {}^3P_0$	11520·5		37153·3		9288·3	
		68·8		*111·3*		
P_1	11451·7		37042·0		9260·5	1·93
		214·0		*435·5*		
P_2	11237·7		36606·5		9151·6	

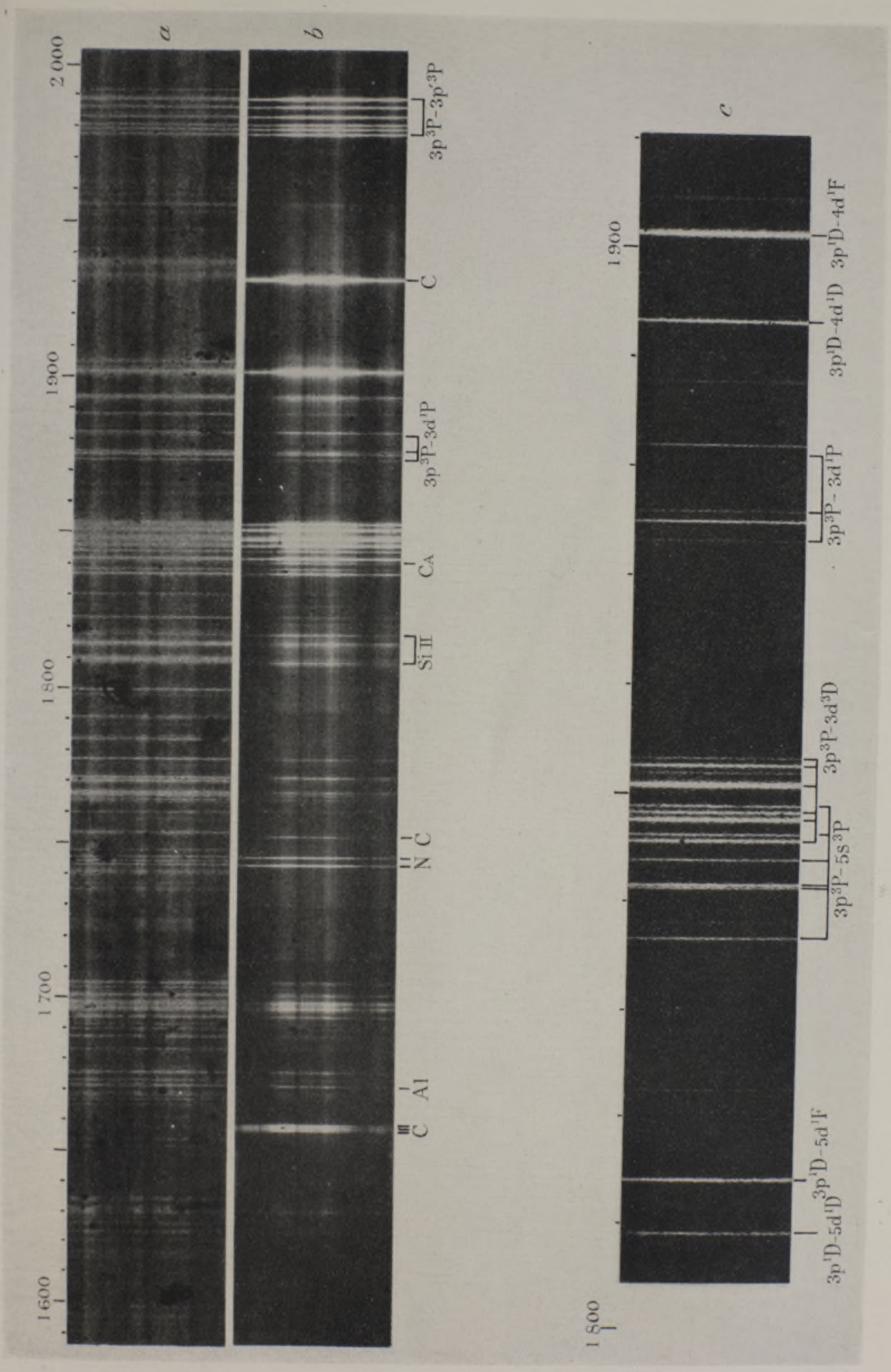
shown divided by four, for readier comparison with Si I. The last column of the table indicates the ratio of the total separations (${}^3P_0 - {}^3P_2$, etc.) in the two spectra. The P II terms, it should be remarked, have been deduced from $3s\ {}^3P$ and $4s\ {}^3P$ by an uncorrected Rydberg formula, but as this series in Si I is nearly Rydbergian, Bowen's values are probably not far from correct.

Apart from the $3p'$ terms, the terms of the two spectra exhibit the kind of relation which has been found in other comparisons of the spectrum of a neutral atom with that of the singly-ionised atom of next higher atomic number. Thus, while the reduced values of the p and s terms of P II are much smaller than those of Si I, the d terms are the greater in P II. It will be seen also that the total triplet separations are not far from twice as great in P II as in Si I.

The $3p'$ terms in the two spectra, however, show striking differences. Whereas in Si I these terms are considerably smaller than $4s\ {}^3P$, in P II they are considerably greater. The ratios of the separations are also very different from those of all the other terms. The only apparent resemblance of the $3p'$ terms in the two spectra is the inversion in $3p'\ {}^3P$.

Summary.

By passing an arc in nitrogen at atmospheric pressure, and using a vacuum spectrograph, the arc spectrum of silicon has been photographed to about



Arc Spectrum of Silicon, λ 1600 — λ 2000.

λ 1600. Many previously unrecorded lines have been observed and the analysis of the spectrum has been greatly extended. Most of the deeper terms predicted by Hund's theory have been identified, and several sequences of singlet and triplet combinations are available for the determination of term values. The deepest term, $3p\,^3P_0$, has been assigned the value 65765, representing an ionisation potential of 8·12 volts. Comparison with singly-ionised phosphorus, P II, shows the general similarity expected, but the terms arising from the electronic configuration sp^3 are relatively much greater in P II than in Si I.

The author's thanks are due to Mr. E. W. H. Selwyn for his suggestion of the method adopted for obtaining arcs in nitrogen, and for his skilful manipulation of the vacuum spectrograph. Mr. Selwyn was enabled to assist in the investigation by a grant from the Department of Industrial and Scientific Research.

DESCRIPTION OF PLATE 18.

(*a*) Arc spectrum of elementary silicon, λ 1600–λ 2000.
(*b*) Arc spectrum of potassium fluo-silicate, λ 1600–λ 2000.
(*c*) Arc spectrum of elementary silicon, λ 1800–λ 1900.

(*a*) and (*b*) were taken in the first order of a 1-metre metal grating, 15,000 lines per inch. The reproduction represents an enlargement of the original negatives by 7½ times.

(*c*) was taken in the first order of a 1-metre glass grating, 30,000 lines per inch. Enlarged 13 times in the reproduction.

In conclusion, the writer desires gratefully to thank Lord Rutherford for his continued encouragement and interest in the work, and for granting facilities for carrying it out at the Cavendish Laboratory. He also desires to express his thanks to the British Thomson Houston Company, Rugby, for a gift of thyratrons, without which it would not have been possible to carry out the tests described.

The Spectrum of the Flame of Carbon Disulphide.

By A. Fowler, D.Sc., F.R.S., Yarrow Research Professor of the Royal Society, and W. M. Vaidya, B.Sc., Imperial College, South Kensington.

(Received May 14, 1931.)

[Plates 14, 15.]

Introductory.

The present investigation of the spectrum of the flame of carbon disulphide was undertaken in the hope that further light might be thrown on the process of combustion of this substance. Extensive experiments have been made in the past, chiefly relating to explosions of mixtures of carbon disulphide and other gases, but a perusal of the literature suggests that the nature of the reactions which take place in such experiments, or in the ordinary flame itself, is still somewhat obscure.*

In connection with such experiments as have been made by chemists, the only reference to observations with the spectroscope seems to be that made by Dixon and Russell,† who stated that when CS_2 was burnt in a Smithell's flame separator, an apparently continuous spectrum was yielded by both the inner and outer cones. On the other hand, the spectrum of the CS_2 flame has been described by several spectroscopists, but the records have been incomplete and further observations seemed to be desirable. In particular, observations over a greater range of spectrum seemed to be necessary, as well as more exact measurements of the bands already known to be emitted. With such extended observations it appeared possible that our present knowledge of the band spectra associated with molecules of sulphur and carbon, and some of their compounds, might aid in tracing the reactions which precede the formation of the final products of combustion.

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* Bone and Townend, "Flame and Combustion in Gases," chap. 33 (1927).

† 'J. Chem. Soc.,' vol. 75, p. 600 (1899).

The earlier observations have been summarised in Kayser's 'Handbuch' (vol. 6, p. 419, 1912). The spectrum of burning sulphur is there described as continuous, an increase in the supply of oxygen resulting in the appearance of a number of bands, apparently identical with those observed by Hartley, and by Eder and Valenta, when sulphur was burnt in the oxy-coal-gas flame, and by H. W. Vogel in a flame of mixed carbon disulphide and nitric oxide. Eder and Valenta* gave the wave-lengths of these bands as 4653, 4610, 4565, 4525, 4485, 4433, 4193, 4160, 4080, 4044, 3938, 3833. These were at first considered to be identical with bands which appear in the vacuum tube spectrum of sulphur, but it was afterwards recognised that there were important differences.

It had also been discovered that the same spectrum of bands was given by sulphur, carbon disulphide, and sulphuretted hydrogen, whether burning singly in air, or mixed with hydrogen, oxygen or nitric oxide. It should be noted, however, that the observations in question were restricted to the blue and violet parts of the spectrum.

Observations of the CS_2 flame in the infra-red by Coblentz† revealed an emission band at $7 \cdot 45\ \mu$, which was identical in position with an absorption band of sulphur dioxide; while less intense bands at $2 \cdot 7\ \mu$ and $4 \cdot 35\ \mu$ were found to correspond with emission bands of carbon dioxide, arising, in part, from the combustion of the lamp wick.

In the course of their observations of substances excited by active nitrogen Strutt‡ and Fowler§ found that while the spectrum of sulphur vapour excited in this way appeared to have nothing in common with that of sulphur in a vacuum tube, it was closely related to that of the flame of carbon disulphide burning in air. The flame, however, gave a much stronger continuous spectrum than the active nitrogen source, and bands of the latter more refrangible than λ 3400 were much less developed in the flame. The chief bands of the CS_2 flame were placed by Strutt and Fowler at about λλ 4480, 4440, 4310, 4275, 4200, 4160, 4080, 4050, 3940, 3835, 3740, 3680, 3645, 3590, 3557, 3500, 3420 and 3370, in general agreement with Eder and Valenta in the region common to the two sets of observations. The origin of the flame bands was not then determined, but their occurrence in the flames of sulphur and sulphuretted hydrogen might have been taken as an indication that carbon was not involved in their production.

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* 'Atlas Typischer Spektren,' p. 20 (1911).

† 'Phys. Rev.,' vol. 24, p. 72 (1907).

‡ Now Lord Rayleigh.

§ 'Proc. Roy. Soc.,' A, vol. 86, p. 111 (1912).

The numerous experiments which have been made in the course of the present investigation have led to the conclusion that the characteristic flame bands mentioned above are due to molecular sulphur, S_2. Many of the bands which have been found in the ultra-violet are also due to S_2, while fainter bands in this region are to be attributed to sulphur monoxide, SO. Sulphur dioxide reveals its presence in some of the experiments by strong absorption bands in the ultra-violet. The spectrum of the "phosphorescent flame" of CS_2 has been found to include bands of sulphur, sulphur monoxide, and carbon monosulphide.

Reference Spectra.

It will facilitate description and interpretation of the various observations if reference be made first to the spectra with which comparisons have been necessary.

The Vacuum Tube Spectrum of Sulphur.—The vacuum tube spectrum of sulphur consists of a succession of fairly close bands, fading towards the red, and extends from the red to about λ 2829, at which point it usually terminates somewhat abruptly. An excellent photograph, taken with a 1-metre grating, has been given by Hagenbach and Könen,* and a list of corresponding wavelengths by Könen is given in Kayser's 'Handbuch,' vol. 6, p. 421 (1912). Photographs with moderate and large dispersion, over the range λ 4800 to λ 3300, showing a large amount of detail, have also been published by Eder and Valenta,† who have tabulated a very large number of the component band lines. For convenience of reference, photographs of the vacuum tube spectrum with an uncondensed discharge, are reproduced in Plate 15, *a* and *b*. It will be seen that the spectrum may be divided into three parts :—

(1) Red to about λ 4700 ; bands nearly evenly spaced.
(2) λ 4700 to λ 3000 ; more complex band groups.
(3) λ 3000 to λ 2829 ; evenly spaced bands.

Absorption Spectrum of Sulphur Vapour.—The absorption spectrum of sulphur vapour has been studied by several observers. J. I. Graham‡ observed two groups of bands, which he distinguished as the A and B groups, extending respectively from λ 4775 to λ 3985 and λ 3415 to λ 2620. Bands of group A were attributed by Graham to the molecule S_8 and those of group B to the molecule S_2, but it now appears that this interpretation is incorrect, all the bands being assignable to S_2.

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* 'Atlas of Emission Spectra,' Plates 25 and 26 (1905).

† 'Denks. Wien. Akad.,' vol. 67, p. 97 (1898).

‡ 'Proc. Roy. Soc.,' A, vol. 84, p. 311 (1910).

Observations of the absorption bands of sulphur vapour at different temperatures have also been recorded by Dobbie and Fox,* but their results do not appear to have any immediate bearing upon the present investigation.

More detailed observations of the absorption of the vapour, in a tube 5 cm. in length, at temperatures ranging from 100 to 1000° C., were afterwards made by Henri and Teves.† According to these observers, at pressures less than 10 mm. and temperatures below 250° C., the vapour consists of S_8 and S_6 molecules, giving only continuous absorption, while above 250° S_2 appears with increasing proportion as the temperature is raised and yields a large number of bands. At a pressure of 0·05 mm., the bands extended from λ 2927 to λ 2713, and as the pressure was increased the number of bands increased very rapidly, extending to λ 2475 on the ultra-violet side, and to λ 3700 towards the red with a pressure of 53 mm.

A vibrational analysis of the system was made by Rosen,‡ as a result of the study of the spectra in absorption and in "white-light fluorescence," in conjunction with a study of the progressions of lines in the fluorescence excited with a quartz mercury lamp (the so-called "resonance spectrum"). Absorption bands were roughly measured over the range λ 3565 to λ 2548, and the fluorescence bands from λ 5720 to λ 2920. The fluorescence bands appear to have been, in the main, identical with bands which occur in the vacuum tube spectrum.

The general appearance of the absorption bands may be gathered from Plate 14, *k*, which was taken with a quartz spectrograph of moderate dispersion, sufficient to show some of the fine structure.

Absorption of Sulphur Dioxide (SO_2).—SO_2 exerts a powerful absorption and exhibits three groups of bands in the ordinary range of observation with a quartz spectrograph. Garratt and Baly§ measured 20 bands between λ 3182 and λ 2802, 21 between λ 2789 and λ 2427, and 14 between λ 2334 and λ 2107. The first of these groups was afterwards observed with greater dispersion by Dr. Frances Lowater.‖ Henri¶ has placed the first and second of Garratt and Baly's groups in a single group, and has suggested the following division :—

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* 'Proc. Roy. Soc.,' A, vol. 95, p. 484 (1919).

† 'Comptes Rendus,' vol. 179, p. 1156 (1924).

‡ 'Z. Physik,' vol. 43, p. 69 (1927) and vol. 48, p. 545 (1928).

§ 'Phil. Mag.,' vol. 31, pp. 505, 512 (1916).

‖ 'Astrophys. J.,' vol. 23, p. 324 (1906).

¶ 'Nature,' February 22, 1930.

(1) λ 3900 to λ 3400 ; appears at 1 atmosphere or more in a tube of 100 cm.
(2) λ 3370 to λ 2450 ; begins to appear at pressure of 0·1 mm.
(3) λ 2350 to λ 2000 : appears at pressures of 0·02 to 10 mm.

The first of these groups has not been of sufficient intensity to be noted in any of the experiments made during the present investigation, but the second (Plate 14, *b*, *c*, *d*) and third groups have appeared strongly as absorption bands in some cases. The second absorption group has also been observed sometimes in ordinary end-on vacuum tubes containing SO_2.†

Emission Bands of Sulphur Monoxide (SO).—The well-marked bands which appear in vacuum tubes containing SO_2 have been measured, and a vibrational analysis given by Henri and Wolff.‡ The spectrum consists of bands fading towards the red, and extends from the violet end of the visible region to λ 2400 in the ultra-violet. Over this range there are more than 40 band-heads distributed regularly at intervals of 40 to 60 A. The structure of this spectrum shows that it originates in molecules of SO. The wave-lengths and intensities of the bands, compiled from Henri and Wolff's data, are as follows :—

3941·6 (0)
3903·6 (1)
3862·7 (3)
3811·8 (5)
3761·6 (2)
3724·7 (3)
3676·2 (7)
3628·2 (3)
3548·7 (6)
3502·1 (4)
3428·1 (3)
3383·2 (6)
3314·8 (1)
3271·0 (10)
3247·5 (1)
3164·7 (10)
3064·1 (10)
3007·9 (2)
2968·4 (5)
2915·4 (4)
2877·4 (4)
2827·8 (8)
2791·0 (2)
2779·9 (1)
2744·3 (6)
2708·6 (1)
2699·4 (4)
2664·8 (5)
2655·7 (1)
2630·1 (1)
2622·2 (3)
2589·0 (2)
2581·1 (1)
2555·5 (0)
2548·6 (2)
2516·4 (1)
2510·4 (1)
2477·7 (1)
2442·0 (1)

Henri and Wolff have concluded that the triatomic SO_2 molecule is broken up by the discharge into an active molecule SO* and an atom of O, the SO bands being emitted on the return of the SO* molecule to its normal state.

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† This absorption probably accounts for the group of bands observed in a vacuum tube of SO_2 by Johnson and Cameron ('Proc. Roy. Soc.,' A, vol. 106, p. 208 (1924)) and described by them as an emission spectrum corresponding with SO_2 absorption as observed by Miss Lowater.

‡ 'J. Physique,' vol. 10, p. 95 (1929).

Carbon Monosulphide (CS).—An ultra-violet band spectrum observed by L. C. Martin† in vacuum tubes containing CS_2, and in the sulphur-carbon arc, was attributed by him to carbon monosulphide. This has since been confirmed by the analysis of the spectrum which has been made by W. Jevons.‡ The spectrum includes a considerable number of well-marked bands, fading towards the red and occupying the region λ 2837 to λ 2436. The strongest bands are at λλ 2693, 2678, 2662, 2606, 2591 and 2579.

Carbonyl Sulphide (COS).—Dixon and Russell included COS among the products of explosions of mixtures of CS_2 and O_2, and also as a constituent of the interconal gases when CS_2 was burnt in a Smithell's separator. As no record of spectroscopic observations of this substance could be found, it was considered desirable to make experiments to ascertain if it gave any characteristic bands, by which its presence in, or absence from, the CS_2 flame might possibly be determined. The substance was prepared by the action of sulphuric acid on potassium thiocyanate in accordance with the method described by Roscoe and Schorlemmer,§ in which it was obtained as a white solid by condensation at the temperature of liquid air. The boiling point of COS under atmospheric pressure is — 47° C.

The COS vapour was introduced into a vacuum tube in the usual manner and was excited to luminosity by the use of a small induction coil. Photographs of the spectrum were taken over the range λ 2000 to λ 5700.

With a fresh supply of COS the discharge was bright blue and the spectrum was a complicated one, consisting of strong bands of CS and S_2, with bands of CO (Ångström bands, etc.) of moderate intensity, while bands of SO were extremely faint or absent. In addition, there was a group of bands, fading towards the violet, which could not be identified and may provisionally be attributed to COS. These bands form a regular system, having the following roughly approximate wave-lengths and wave-numbers :—

λ.	ν.	Δν.
3077	32490	
		363
3043	32853	
		371
3009	33224	
		368
[2976]*	33592	
		377
2943	33969	
		373
2911	34342	
		370
2880	34712	

* Falls in a CO group.

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† 'Proc. Roy. Soc.,' A, vol. 89, p. 127 (1913).

‡ 'Proc. Roy. Soc.,' A, vol. 117, p. 351 (1927).

§ 'Treatise on Chemistry,' vol. 1, p. 831 (1911).

The spectrum of S_2 observed in the blue discharge through COS, especially in the wider parts of the tube, was somewhat less complex than that of the S_2 vacuum tube, and the characteristic flame bands were more prominently displayed. Sulphur was copiously deposited on the walls of the tube.

When the discharge had passed for some time the glow became much whiter. The bands of CS remained strong, but those of S_2 were much reduced in intensity; bands of CO were much strengthened and bands of SO were also observed, though they were not at all conspicuous. The absence, under these conditions, of the bands provisionally assigned to COS gives support to the origin suggested for them.

From these experiments it appears possible that the above group of bands would serve for the detection of COS in the CS_2 flame if it were present.

Spectrographs Employed.

Most of the photographs for the present investigation were taken with one of Hilger's small quartz spectrographs (E31). Though the dispersion is small, it is quite adequate for the comparison of the spectra of the various sources, and the use of such an instrument results in a great saving of time. Most of the measurements, however, were made on photographs taken with a larger quartz spectrograph (E2), using the copper or iron arc as a reference spectrum. Photographs of the CS_2 flame and S_2 vacuum tube spectra with greater dispersion and resolution, covering the region λ 3200 to λ 6100, were also obtained in the first order of a 1-metre concave grating. These served to give good measures of many of the bands, but in some cases the increased resolution made it impossible to determine the precise positions of the heads of the bands.

CS_2 *supported by* O_2.

The experimental results are not here presented in the order in which they were obtained, but in the order which it is believed will make them most clearly understood. For this reason it will be convenient to begin by describing the results obtained with a CS_2 flame into which oxygen was blown through a small jet near the base of the flame, as indicated in the figure. For producing the flame it was found sufficient to put the liquid CS_2 into the bowl of an ordinary spirit lamp provided with a cotton wick.

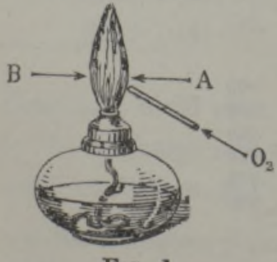


FIG. 1.

Observations in Direction A.—When oxygen was blown into the flame, and observations made in the direction A, the spectrum obtained—apart from the bright continuous spectrum—consisted wholly of emission bands fading towards the red, and extending from the red to the limit of the range of observation about λ 2200. From the red to about λ 4700 (Plate 15, *d*), the bands appeared to be identical with the corresponding part of the vacuum tube spectrum (Plate 15, *a*). From λ 4700 to about λ 3100 (Plate 14, *a*), the spectrum was much simpler than that of the vacuum tube (Plate 15, *b*), consisting of the most characteristic flame bands which have already been specified. Several strong tube bands do not appear in the flame spectrum, and some of the flame bands are either absent from or very feeble in the tube spectrum. Beyond λ 3100 the flame and tube spectra are practically identical as far as λ 2829. From λ 2829 downwards the flame bands are identical with sulphur bands observed in absorption (group B of Graham), but beyond λ 2700 these bands are blended with bands of SO previously tabulated, and observed as far as λ 2442.

It will be seen that the most characteristic part of the spectrum of the CS_2 flame, when observed in the above way, lies in the blue and violet between λ 4700 and λ 3100, in which region the spectrum is quite different in appearance from the tube spectrum, although some bands are common to the two sources (Plate 15, *c*, *c′*). The vibrational analysis which is given later, however, shows quite clearly that these characteristic flame bands can be arranged in a single system with the less refrangible and more refrangible groups of bands as constituent parts, and since the latter are undoubtedly due to S_2, it follows that the characteristic flame bands are also due to S_2 molecules.

All the bands of the flame spectrum as observed in this way are thus accounted for by S_2 and SO. There are no indications of Martin's bands of CS, nor of the group of bands which have been provisionally attributed to COS. The presence of SO_2 as a product of combustion, however, is shown in some of the experiments described later.

Observations in Direction B.—When the oxygen-fed flame was observed in the direction marked B in fig. 1, the spectrum as a whole remained the same, but the sulphur bands extending from λ 3291 to λ 2570 appeared as strong *absorption* bands, the maximum intensity occurring about λ 2770 (Plate 14, *g*, *k*). All of these bands showed rotational fine structure with the dispersion of Hilger's E2 quartz spectrograph. Between λ 3291 and λ 3500 the bands observed in direction B were very feeble, as if emission and absorption were mutually destructive. Photographs showing the reversed bands have been very helpful in distinguishing the S_2 bands from those of SO in the region where they overlap when the flame is observed in direction A.

The Flame in an Atmosphere of O_2.—In the first instance, the experiments on the CS_2 flame supported by oxygen were made with the flame enclosed in a glass chimney, into which a slow stream of oxygen was passed. The chimney was provided with a side tube closed with a quartz window, so as to permit observations in the ultra-violet.

Under these conditions, the spectrum from the visible to the near ultra-violet was the same as that already described, but the predominant feature in the ultra-violet was the absorption spectrum of SO_2, arising from the accumulation of this gas in the chimney (Plate 14, *c*). The second group of bands described by Henri, extending from λ 3370 to λ 2450, appeared very strongly, and the third group, below λ 2350 also appeared when sufficiently long exposures were given. In the range of spectrum investigated, these and similar observations provide the only spectroscopic evidence of the production of SO_2 in the process of combustion of CS_2.

Carbon Disulphide burning in Nitrous Oxide.

Experiments similar to those made with oxygen were repeated with the substitution of N_2O as the supporter of combustion. When burnt in a chimney, the spectrum was similar to that observed with oxygen, but the continuous spectrum was possibly less intense relatively to the bands in the blue (Plate 14, *b*). Under these conditions, bands of SO also appeared in the region λ 2600 to λ 2400. When a jet of nitrous oxide was directed on to the flame, absorption bands of S_2 were observed as in the corresponding experiment with oxygen.

CS_2 *burning in Air.*

The flame of CS_2 when burning in the ordinary way in air showed a spectrum (Plate 14, *e*) very similar to that of the flame when oxygen was blown in and observations made in the direction B of fig. 1. That is, the S_2 bands in the green, yellow and red, and the more characteristic flame bands of S_2 in the blue and violet, appeared as emission bands, while the more refrangible bands appeared in absorption. To bring out the latter feature, exposures of the photographic plates were somewhat prolonged. Beyond the absorption bands there were faint indications of the emission bands of SO which occurred in the oxygen-fed flame. No indications of the CS or " COS " bands were found in these observations.

It would thus appear that with the restricted supply of oxygen provided by ordinary air, the sulphur vapour arising from the decomposition of CS_2 in the flame was not quickly consumed to form SO_2, but accumulated in sufficient quantity around the flame to produce the observed absorption of S_2 bands in the ultra-violet. As previously noted by others, a heavy deposit of sulphur was obtained when a cold surface was inserted in the flame, but no deposit of carbon.

When the CS_2 was burnt in air, inside a chimney, the spectrum (Plate 14, *d*) showed the usual flame bands from the visible to the near ultra-violet, but the SO_2 absorption bands of Henri's second group came out very strongly, obliterating the S_2 absorption bands and the remainder of the ultra-violet.

Further experiments on the CS_2 flame in air were made with a Smithell's separator, which permitted independent observations of the inner and outer cones. In place of the usual two concentric tubes with the inner one fixed on a burner, it was found convenient to use the burner itself for the inner cone, so that only one tube was necessary. This tube was of silica glass, 7 cm. in length and 1·5 cm. in diameter, and the burner was of the "micro-burner" type, giving only a small flame. By means of a water pump and a large jar, air under a small pressure was bubbled gently through carbon disulphide, heated to 27° C., and thence to the micro-burner. With suitable adjustment of the air regulator and of the height of the silica tube, the flame was readily separated into two cones, which burned very steadily. With this arrangement, the outer cone was about 4 cm. in length and the inner one 2 cm. To avoid undue accumulation of SO_2 in the space surrounding the inner cone, the silica tube was provided with a short side tube in the direction of the spectrograph, this tube being left open to the air. There was a striking difference in the appearance of the two cones, the outer one being pale blue and not very luminous, while the inner one was of a lilac colour and considerably brighter than in the ordinary flame in air.

The outer cone gave a spectrum which was not distinguishable from that of the normal flame in air. That is, it showed the characteristic emission bands of S_2 in the blue and near ultra-violet, absorption bands of S_2 in the ultra-violet, feeble indications of SO bands, and a fairly strong continuous spectrum.

The inner cone also showed the characteristic flame bands, but differed from the outer cone in showing the S_2 bands in the ultra-violet in emission, as in the flame fed with oxygen and viewed in the direction A of fig. 1. The emission bands were traced as far as λ 2900, and beyond this there were feeble indications of SO bands. The continuous spectrum was fairly strong and appeared to be relatively stronger in the visible spectrum as compared with the continuous spectrum given by the outer cone.

Other Sources of Flame Bands.

Sulphur Arc in Air.—In his investigations of the bands of carbon monosulphide, Martin included observations of the spectrum of sulphur in the carbon arc. Successful results were obtained by using a hollow carbon well charged with sulphur as the upper (positive) pole, which secured a steady flow of sulphur into the arc. In addition to bands of carbon and cyanogen, the spectrum showed faint bands of sulphur and the bands of carbon monosulphide. By surrounding the arc with sulphur vapour from a test-tube in which sulphur was boiled, the intensity of the monosulphide bands was increased, and sulphur bands from λ 2800 towards the red appeared as absorption bands.

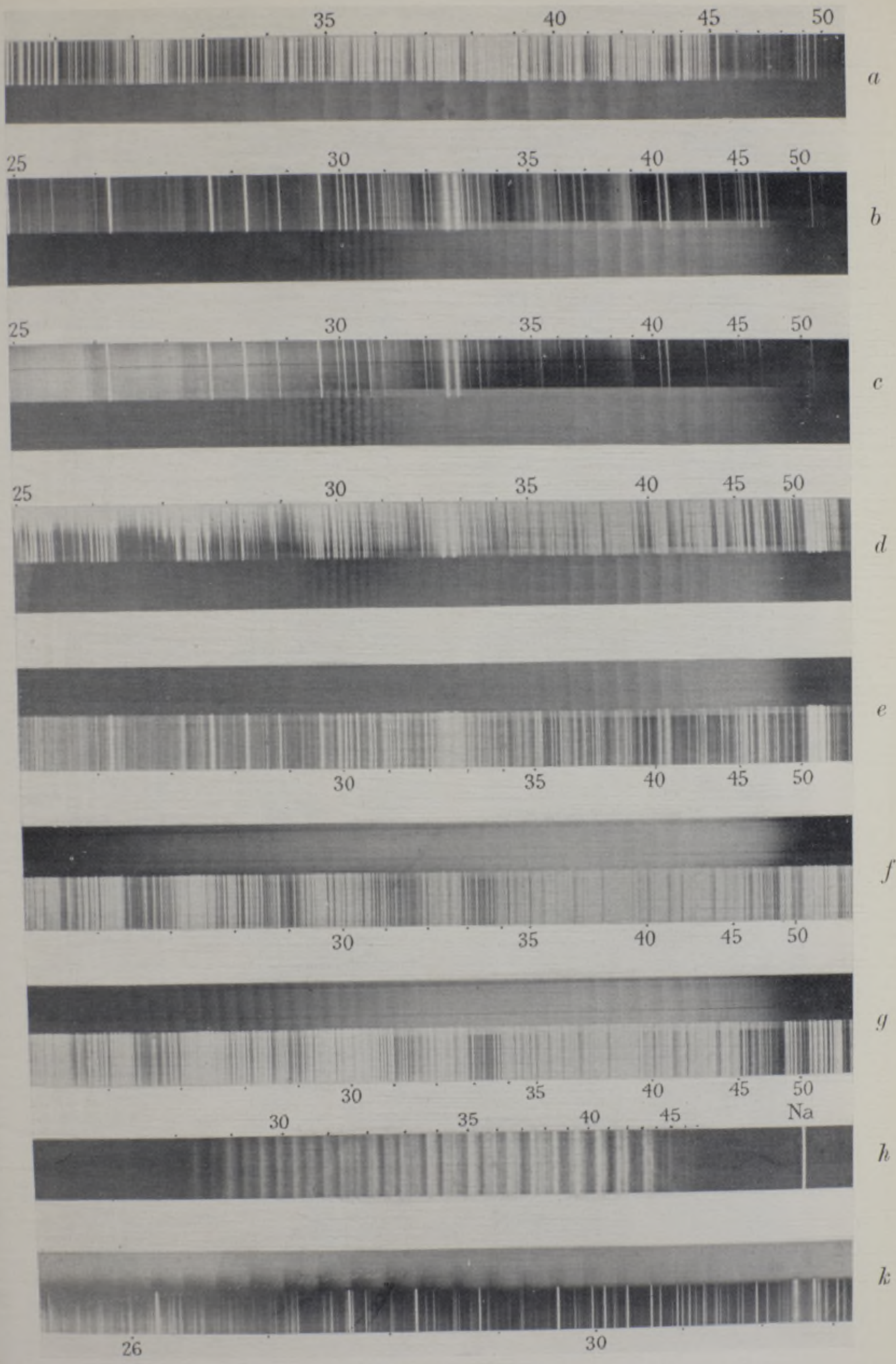
A further examination of Martin's photographs, which were taken at the Imperial College, has revealed the additional fact that the characteristic CS_2 flame bands in the region λ 4700 to λ 3400 were quite prominent in the arc spectrum, so far as they were not obscured by bands of carbon and cyanogen. The reversed bands of sulphur extended considerably further towards the red than those which appear in the flame, namely, to the band λ 3417. The sulphur bands on the red side of the more characteristic flame bands were also fairly well developed in the arc.

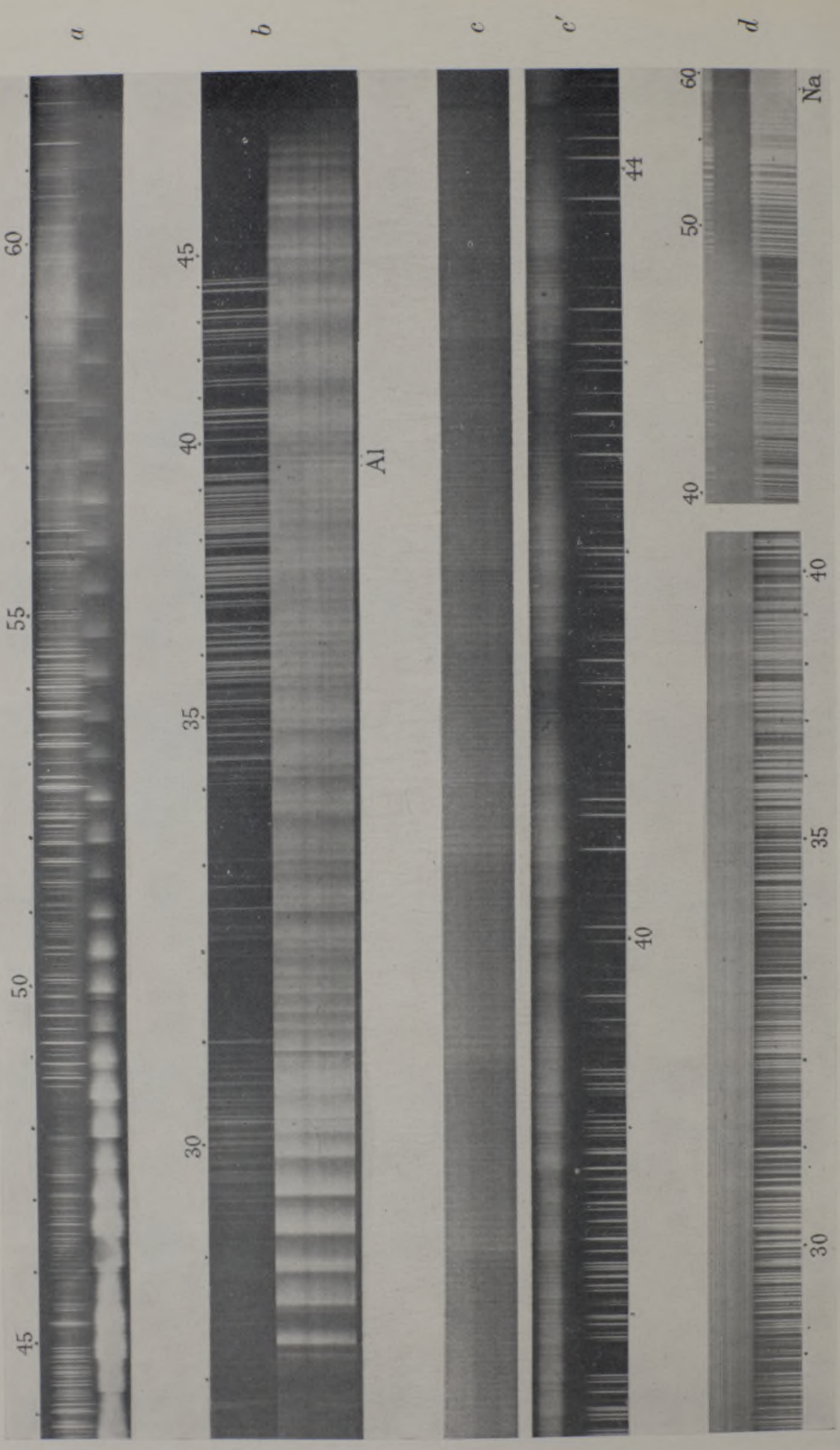
Thus, the spectrum of sulphur produced in the arc is essentially identical with that of the CS_2 flame in air, or with that of the flame fed with oxygen and observed in the direction B shown in fig. 1. The greater encroachment of the ultra-violet absorption bands towards the red is probably to be attributed to the higher temperature of the arc.

The Flame of Burning Sulphur.—The pale blue flame of sulphur burning in air shows the characteristic bands of the CS_2 flame in the blue and violet, but they are somewhat indistinct on account of the greater brightness of the continuous spectrum. In addition, as noted by Strutt and Fowler (*loc. cit.*, p. 112), there is another group of bands in the region λ 3200 to λ 3000, which there is now no difficulty in identifying with absorption bands of SO_2. The continuous spectrum extends far beyond λ 3200 and shows feeble indications of the emission bands of SO.

When the sulphur flame was intensified by burning in a chimney supplied with oxygen, the spectrum only appeared to differ from that of the flame in air in the greater intensity of the SO_2 absorption.

Flame of Hydrogen Sulphide (H_2S).—In addition to the characteristic flame bands of CS_2, the flame of H_2S showed the band of HO at λ 3064. Otherwise,


35 40 45 50
a
25 30 35 40 45 50
b
25 30 35 40 45 50
c
25 30 35 40 45 50
d
e
30 35 40 45 50
f
30 35 40 45 50
g
30 35 40 45 50
30 35 40 45 Na
h
k
26 30


a
45
50
55
60
b
30
35
40
45
Al
c
c′
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44
d
30
35
40
40
50
60
Na

the spectrum was similar to that of burning sulphur, except that SO_2 absorption was less developed.

Sulphur in Active Nitrogen.—The blue glow of sulphur vapour in active nitrogen was found by Strutt and Fowler to give a spectrum closely related to that of CS_2 burning in air. But whereas bands more refrangible than λ 3400 were very feeble in the flame, they were well developed in active nitrogen as far as λ 2800, where the spectrum ended abruptly, as in the vacuum tube. The active nitrogen source was also remarkable for the practically complete absence of continuous spectrum. One of the photographs, taken with small dispersion, is reproduced in Plate 14, *h*.

A re-examination of the photograph has confirmed the foregoing description. Except for the feebler continuous spectrum, the active nitrogen source is similar to that of the CS_2 flame fed with a jet of oxygen and viewed in the direction A of fig. 1. That is, the spectrum consists of a continuous succession of emission bands of sulphur. Strutt and Fowler's statement that this spectrum has nothing in common with that of the sulphur vacuum tube, however, requires amendment. Beyond λ 3400 the bands are all present in the vacuum tube spectrum, and some of those between λ 3400 and λ 4700 are also observed in the tube. The general appearance of the spectrum in the latter region, however, is very different from that of the vacuum tube (compare *c* and *c′*, Plate 15).

CS_2 *in Active Nitrogen.*—Two groups of bands were observed by Strutt and Fowler in the spectrum given by CS_2 in active nitrogen. The first consisted of the characteristic flame bands, which, however, were only well developed on the red side of λ 3700. The second group consisted of bands, also degraded to the red, occurring in the region λ 2920 to λ 2550. These bands also appeared in the vacuum tube spectrum of impure SO_2 and it is now perfectly clear that they were identical with SO bands tabulated by Henri and Wolff. This will appear from the following comparison of wave-lengths :—

λ (S. & F.).	λ SO.	λ (S. & F.).	λ SO.
2920	2915·4 (4)	2665	2664·8 (5)
2830	2827·8 (8)	2620	2622·2 (3)
2785	2779·9 (1)	2592	2589·0 (2)
2745	2744·3 (6)	2550	2548·6 (2)
2700	2699·4 (4)		

The wave-lengths given by Strutt and Fowler were only considered as rough approximations, so that the agreement is satisfactory. Further, direct photographic comparisons of the spectrum with that of the SO_2 tube have left no doubt as to the identity of the two sets of bands. Beyond λ 3837 the intensity of the sulphur bands falls off very rapidly in the active nitrogen source, and the spectrum then consists almost entirely of the bands of SO.

It should perhaps be recalled that traces of oxygen or some other substance are necessary for the production of the afterglow of nitrogen,* so that there is no difficulty in accounting for the presence of SO molecules in the reaction of the nitrogen with carbon disulphide.

It may be further noted that in this source the only spectroscopic evidence of the presence of carbon is that afforded by a weak band of CN at λ 3883.

The Phosphorescent Combustion of CS_2.

As first recorded by G. S. Turpin,† the vapour of CS_2 may be made to glow without bursting into flame by passing the vapour into a heated flask. Under these conditions Turpin observed that a reddish-brown volatile substance containing carbon and sulphur was deposited and that SO_2 was produced in abundance, while there was little, if any, CO or CO_2. Dixon and Russell‡ afterwards found that the glow could be maintained indefinitely by passing a stream of air and oxygen over the liquid CS_2 and through a tube heated to 200° C. Extensive experiments on the slow combustion of CS_2 and other substances, by the heated tube method, have also been made by Gill, Mardles and Tett§ in the Air Ministry Laboratory, but no spectroscopic observations appear to have been attempted.

The first records of the spectrum of the phosphorescent glow were obtained by H. J. Emeléus|| in Professor Baker's laboratory at the Imperial College. Even with small dispersion and rapid plates, very long exposures, ranging from 40 to 250 hours, were found necessary to give photographs of sufficient density.

Further investigations of this spectrum have been commenced, but it seems desirable meanwhile to state the general results of a re-examination of Emeléus's plates, which have been kindly placed at our disposal by Professor Baker. As described by Emeléus, the spectrum of the CS_2 glow consists of two groups of bands shaded to the red, one in the blue and violet extending from λ 4530

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* R. J. Strutt, 'Proc. Roy. Soc.,' A, vol. 91, p. 303 (1915).

† 'Brit. Assoc. Rep.,' 1890, p. 776.

‡ 'J. Chem. Soc.' vol. 75, p. 600 (1899).

§ 'Trans. Faraday Soc.,' vol. 24, p. 574 (1928).

|| 'J. Chem. Soc.,' vol. 128, p. 2948 (1926).

to λ 3400, and the other in the ultra-violet, occupying the range λ 3100 to λ 2485. The region intermediate between the two groups is apparently continuous.

The first group was observed by Emeléus to be closely related to the corresponding part of the spectrum of the normal CS_2 flame. This has been confirmed by direct comparison of photographs of the two sources. It has been noted, however, that certain bands which occur in the flame are relatively weaker in the glow, the bands which retain their intensity being chiefly those which fall in the uppermost row ($v' = 0$) of the table showing the vibrational analysis of the flame bands which is given later (Table II). This simplification is presumably associated with the lower temperature of the phosphorescent glow.

The second group of bands, as appears from the photographs reproduced by Emeléus, is not much less intense in the glow than the first group, whereas it is very feeble in the ordinary flame. From re-measurements of the plates, and by direct comparison with the SO spectrum as given by a vacuum tube containing SO_2, it resulted that many of the bands of the second group were identical with Henri and Wolff's bands of SO. This conclusion, as was afterwards found, had already been reached by V. Kondratjew,* in a comparison of the observations of Emeléus with those made by himself on the glow of sulphur vapour in a heated flask containing oxygen at a low pressure. Some of Kondratjew's identifications with bands of SO, however, were based only upon calculations from Henri and Wolff's formula for the SO bands, and are probably incorrect. Emeléus's second group actually consists of bands of SO, fading out considerably after λ 2800, with bands of CS superposed upon them. The latter naturally do not occur in Kondratjew's photographs of the sulphur glow and their approximate agreement with calculated bands, not actually observed in the SO spectrum, can only be considered as accidental.

Numerical details are reserved until additional photographs of the glow spectrum have been obtained, but this preliminary investigation appears to us to have established the presence of bands of S_2, SO and CS in addition to a continuous spectrum of moderate intensity.

Wave-lengths of CS_2 *Flame Bands.*

The wave-lengths, intensities (maximum = 6) and wave-numbers of the heads of bands occurring in the CS_2 flame spectrum are given in Table I. The vibrational quantum numbers, v', v'', of the bands are also indicated.

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* 'Z. Physik,' vol. 63, p. 322 (1930).

Table I.—S_2 Bands in Flame of $CS_2 + O_2$.

(v′v″).	λ Int.	ν.	(v′v″).	λ Int.	ν.	(v′v″).	λ Int.	ν.
(9, 30)	6165·7 (1)	16214	(0, 14)	4523·5 (2)	22101	(2, 2)	3216·1 (2, 2)	3108
(8, 29)	6102·6 (2)	16382	(2, 15)	4478·8 (4)	22321	(4, 3)	3203·2 (2, 2)	3121
(7, 28)	6040·4 (2)	16551	(1, 14)	4433·6 (6)	22549	(3, 2)	3171·5 (2, 3)	3152
(6, 27)	5980·4 (1)	16717	(0, 13)	4395·0 (2)	22747	(5, 3)	3161·1 (1, 1)	3162
(9, 29)	5962·1 (3)	16768	(2, 14)	4355·0 (2)	22956	(2, 1)	3143·7 (1, 1)	3180
(8, 28)	5901·0 (4)	16942	(1, 13)	4311·0 (6)	23190	(4, 2)	3132·4 (3, 4)	3191
(7, 27)	5840·2 (4)	17118	(0, 12)	4274·4 (3)	23389	(3, 1)	3101·5 (1, 3)	3223
(6, 26)	5782·1 (2)	17290	(1, 12)	4193·8 (6)	23838	(5, 2)	3091·7 (5, 4)	3233
(9, 28)	5769·7 (3)	17327	(0, 11)	*4157·2 (5)	24048	(4, 1)	3063·6 (3, 4)	3263
(8, 27)	5709·6 (4)	17510	(1, 11)	4081·0 (3)	24497	(6, 2)	3054·9 (3, 3)	3272
(7, 26)	5651·7 (4)	17689	(0, 10)	*4045·8 (6)	24710	(3, 0)	3033·1 (1, 2)	3296
(6, 25)	5596·1 (3)	17865	(1, 10)	3973 (1)	25160	(5, 1)	3024·8 (4, 5)	3305
(8, 26)	5530·1 (3)	18079	(0, 9)	*3939·1 (6)	25379	(7, 2)	3018·0 (2, 1)	3312
(7, 25)	5472·5 (4)	18268	(2, 10)	3909·6 (1)	25571	(4, 0)	2997·0 (1, 2)	3335
(6, 24)	5418·7 (4)	18449	(0, 8)	*3837·3 (6)	26053	(6, 1)	*2989·7 (4, 4)	3343
(5, 23)	5359·7 (3)	18653	(2, 9)	3811 (1)	26232	(5, 0)	2960·1 (2, 3)	3377
(4, 22)	5309·9 (3)	18828	(0, 7)	*3740·0 (6)	26730	(7, 1)	*2954·2 (4, 4)	3384
(6, 23)	5249·8 (5)	19043	(1, 7)	3677·6 (3)	27184	(6, 0)	2926·6 (2, 5)	3415
(5, 22)	5193·7 (5)	19249	(0, 6)	*3645·2 (5)	27426	(8, 1)	*2920·4 (4, 2)	3423
(4, 21)	5145·5 (4)	19429	(1, 6)	3587·4 (5)	27867	(7, 0)	2892·5 (4, 6)	34562
(3, 20) }	5090·9 (5)	19637	(0, 5)	3555·8 (3)	28115	(9, 1)	2888·1 (4, 2)	34615
(6, 22) }			(1, 5)	3500·5 (5)	28559	(8, 0)	*2860·2 (3, 6)	34952
(5, 21)	5036·8 (6)	19848	(0, 4)	3469·6 (2)	28814	(9, 0)	*2829·3 (3, 6)	35334
(4, 20)	4990·1 (6)	20034	(2, 5)	3451·0 (2)	28969	(10, 0)	2799·0 (3, 6)	35717
(3, 19)	4937·2 (5)	20249	(1, 4)	3417·0 (4)	29257	(11, 0)	2769·6 (3, 6)	36096
(2, 18)	4893·8 (5)	20428	(0, 3)	3387·0 (1)	29516	(12, 0)	2741·0 (–, 6)	36472
(4, 19)	4842·2 (6)	20646	(2, 4)	3369·6 (4)	29669	(13, 0)	2712·9 (–, 6)	36850
(3, 18)	4790·8 (6)	20868	(1, 3)	3336·7 (2)	29961	(14, 0)	2686·2 (–, 6)	37216
(2, 17)	4747·6 (5)	21057	(3, 4)	3321·2 (1)	30101	(15, 0)	2662·0 (–, 6)	37555
(1, 16)	4699·0 (3)	21275	(2, 3)	†3290·7 (3, 2)	30380	(16, 0)	2638·0 (–, 5)	37896
(3, 17)	4651·3 (4)	21493	(1, 2)	3259·9 (2, 1)	30667	(17, 0)	2615·1 (–, 4)	38228
(2, 16)	4610·0 (5)	21686	(3, 3)	3244·7 (3, 3)	30811	(18, 0)	2593·0 (–, 3)	38554
(1, 15)	4563·2 (4)	21908						

* Each of these bands has a fainter head on the more refrangible side.

† The two intensities refer to flame emission and flame absorption as respectively observed in directions A an B of fig. 1.

Note.—Bands of SO are superposed on the S_2 bands from about λ 2700 and extend further into the ultra-viol than the sulphur bands.

In the course of the measurements it was announced that the measurement and analysis of the sulphur bands was in progress in other laboratories,‡ and laborious determinations of high precision were accordingly not undertaken. It is believed, however, that the wave-numbers are sufficiently accurate for a vibrational analysis, and for the present purpose of demonstrating that the most characteristic flame bands in the blue and violet form part of the same system as the bands in the visible spectrum and those in the ultra-violet, both of which are undoubtedly due to S_2 molecules.

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‡ Naudé and Christy, ‘Phys. Rev.,’ vol. 36, p. 1800 (1930); and vol. 37, p. 490 (1931); P. Huber, ‘Phys. Rev.,’ vol. 37, p. 23 (1931).

The wave-lengths from λ 4700 to the limit in the ultra-violet are from measurements of photographs taken with Hilger's E2 quartz spectrograph, using iron and copper arcs as comparison spectra. The resolution of this instrument is not too great to obscure the heads in most of the bands, while the scale is sufficient for the purpose in view. Vacuum tube spectra were used for bands which appeared to be identical in tube and flame. In the region λ 4700 to λ 6165, the bands were measured on plates taken with a 1-metre grating (14438 lines per inch), with the sulphur vacuum tube as source; comparisons of the two sources as photographed with the smaller dispersion of the quartz spectrograph indicated that in this region the tube bands may be confidently taken to represent the flame bands. While many of the band heads are sharply defined in the grating plates, others are less definitely indicated, and in such cases the parts selected for measurement were those suggested by the structure of the band system which is given in the next section.

The intensities are ordinary estimates referring to the *emission* spectrum, as obtained when oxygen was blown into the CS_2 flame and observations made in the direction A of fig. 1. As already pointed out, when such a flame was observed in direction B, or when the source was an ordinary flame of CS_2 burning in open air, many ultra-violet bands appeared in absorption, although in the blue and violet only emission bands were observed. As the relative intensities in emission and absorption were markedly different for some of the bands, it has been thought desirable to give estimates of intensity for both. Thus, from λ 3290 onwards, two intensity numbers are given, the first representing emission and the second absorption. Beyond λ 2769 the emission bands are less distinct and are superposed on bands of SO, and for these only the intensities in absorption are stated. Among the bands which are distinctly stronger in emission than in absorption are λλ 2920 and 2888, while λλ 2997, 2960 and 2926 may be noted as examples of bands which are relatively stronger in absorption than in emission.

Vibrational Analysis of the Flame Bands.

From the general appearance and conditions of occurrence of the most characteristic flame bands in the blue and violet there was a strong presumption that they originated in the same molecules as those which gave rise to the associated bands in the visible and ultra-violet regions. There was apparently no place for several of the flame bands, however, in the scheme for S_2 band heads which had been given by Rosen, and it became necessary to ascertain if the scheme could be extended or modified so as to include them.

It was soon found that all the flame bands could be arranged in a single scheme, which was in general agreement with that of Rosen as regards the ultra-violet bands, but differed from it very considerably for the less refrangible bands. In particular, the new scheme introduces an additional $v'v''$ $(0, v'')$ progression, which includes some of the strongest flame bands, and thus requires that Rosen's v' values should be increased by unity throughout. As a further result of the present work, the scheme has been extended considerably towards the red.

The band system is so much extended in the v'' direction that it cannot conveniently be printed in every detail. The main features, however, are exhibited in Table II, which indicates the *intensities* of the observed bands in relation to the $v'v''$ values. With the aid of Table I, which includes the $v'v''$ for the bands, a complete table may readily be constructed by anyone who requires it.

It will be seen that the flame bands, as arranged in Table II, trace out in a very satisfactory manner a wide-open Condon parabola of intensity distribution, such as would be expected where ω_e' and ω_e'' differ so markedly as they do in the present instance.

As Naudé and Christy* have pointed out, but without giving details, there are several perturbations among the vibrational energy levels of the upper (v') states. This will be seen from Table II, which includes the $\Delta\nu$ of successive bands in the progressions; means have been taken where the observations gave more than one value. On account of these perturbations it is not possible to represent the whole system accurately by a simple formula, but the following may be taken as a fair approximation:

$$\nu_{\text{head}} = 31659 + (432\cdot 3v' - 2\cdot 63v'^2) - (722\cdot 1v'' - 2\cdot 82v''^2),$$

where v' and v'' are the vibrational quantum numbers for the energy levels in the upper (excited) and lower (ground) states of the molecule respectively.

The analysis of Naudé and Christy has further shown that the S_2 system under consideration is due to a $^3\Sigma \rightleftarrows {}^3\Sigma$ transition, and is therefore the counterpart of the well-known Schumann-Runge system of O_2. By analogy with O_2, the spectrum of S_2 would be expected to include another system of bands corresponding with the atmospheric absorption bands of oxygen in the solar spectrum, and representing the transition $^1\Sigma \rightleftarrows {}^3\Sigma$. This, however, would be a faint system and would fall far in the infra-red.

The main result of the analysis, for our present purpose, is the demonstration

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* *Loc. cit.*, and 'Phys. Rev.,' vol. 37, p. 490 (1931).

Table II.—Vibrational Analysis of Flame Emission Bands ($CS_2 + O_2$).

v'' / v'	$\Delta\nu$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	v'' / v'
		722					694					668					634					605					577					554	
0					1	2	3	5	6	6	6	6	5	3	2	2																	0
	447																																
1				2	2	4	5	5	3			1	3	6	6	6	4	3															1
	413																																
2			1	2	3	4	2				1	1				2	4	5	5	5													2
	435																																
3		1	1	2	3	1													4	6	5	5											3
	397																																
4		1	3	3	2																6	6	4	3									4
	418																																
5		2	4	5	1																		6	5	3								5
	389																																
6		2	4	3																				5	5	4	3	2	1				6
	401																																
7		4	4	2																							4	4	4	2			7
	391																																
8		3	4																									3	4	4	2		8
	384																																
9		3	4																											3	3	1	9
	383																																
10		3																															10
	379																																
11 ↓ 18		3																															11

that the characteristic flame bands of carbon disulphide in the blue and violet form part of the system which includes the visible and ultra-violet bands of S_2 and must, therefore, also be attributed to S_2 molecules.

Discussion.

The foregoing observations may be of interest as giving information relating to some of the reactions which precede the formation of the well-known products of combustion, but it seems unlikely that they will give complete answers to all the questions which arise. The observations do not furnish any direct evidence, for example, of the formation, in the first stages, of such complex molecules as are required by the peroxidation theory of combustion.

The simplest flame which has been investigated is that of sulphur. It is possible that in this case the first stages involve molecules of S_8, but unless these are associated in some way with the continuous spectrum, there is no spectroscopic indication of their existence. The spectrum definitely indicates the presence of S_2 molecules, and shows that there is no dissociation into sulphur atoms, which would exhibit a line spectrum. The S_2 molecules are thus merely raised to higher energy levels, and emit their characteristic bands on returning to the normal state. The final product is SO_2, but the spectrum gives indications of SO as an intermediate stage. It does not seem possible, however, to decide from these observations alone whether it is the excited or unexcited S_2 molecules which combine with oxygen to form SO and SO_2.

According to the peroxidation theory, the successive reactions might be expressed as follows :

$$S_2 + O_2 \rightarrow S_2O_2 \rightarrow 2SO$$

$$2SO + O_2 = 2SO_2.$$

Even in the case of sulphur burning in the open air, SO_2 surrounds the flame in sufficient quantity to reveal its presence by absorption bands peculiar to this gas.

In the low-temperature phosphorescent flame of CS_2 there are spectroscopic indications of S_2, SO and CS, the products of combustion being SO_2 and CO_2. The observations might thus be accounted for by the simple equation

$$4CS_2 + 3O_2 = 2S_2 + 2SO + 2CS + 2CO_2,$$

further combinations with oxygen resulting in SO_2 and additional CO_2. According to Gill, Mardles and Tett (*loc. cit.*), however, the primary oxidation product of CS_2 is an active peroxide, CS_2O_2. Assuming this, it may be supposed that the reactions would proceed somewhat as follows :

$$CS_2O_2 + CS_2 \rightarrow 2CS_2O$$
$$4CS_2O + O_2 = 2S_2 + 2SO + 2CS + 2CO_2,$$

the result being the same as that expressed by the simpler equation above.

Under the higher temperature conditions of the flame in air or oxygen, the spectrum differs from that of the phosphorescent flame in the apparent absence of bands of CS and the relatively feebler representation of SO. If it be assumed that CS is not formed in this case, the spectroscopic observations, including Coblentz's infra-red bands of CO_2, would be satisfied by the equation

$$2CS_2 + 3O_2 = S_2 + 2SO + 2CO_2,$$

or, if peroxidation occurs, by the following :

$$CS_2O_2 + CS_2 \rightarrow 2CS_2O$$
$$2CS_2O + 2O_2 = S_2 + 2SO + 2CO_2.$$

The spectroscopic observations appear to give no evidence of the existence of these peroxides in the flames, but it might be unwise to regard this as furnishing a satisfactory proof of their absence.

It is conceivable that CO might be formed as well as CO_2, but the observations are not conclusive on this point. The spectrum of the CO flame consists of weak and ill-defined bands superposed on a bright continuous spectrum,* and it would scarcely be possible to detect its presence when involved in the sulphur bands and continuous spectrum of the CS_2 flame. All that can be said is that since the continuous spectrum is not more intense in the flame of CS_2 than in that of sulphur alone, it is improbable that CO is present in any considerable amount.

Summary.

It has been found that the most characteristic bands of the ordinary CS_2 flame, extending from the blue to the near ultra-violet, form part of the system already known to be due to S_2 molecules and must, therefore, also be attributed to S_2. The ultra-violet bands of S_2 appeared in absorption, but they were obtained in emission when a stream of oxygen was directed on the flame. Emission bands of SO also appeared feebly in the flame spectrum. When the flame was enclosed in a chimney, absorption bands of SO_2 appeared in addition.

Generally similar results were obtained in experiments on the flames of sulphur and hydrogen sulphide, the latter also showing bands of HO.

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* *Cf.* Weston, 'Proc. Roy. Soc.,' A, vol. 109, p. 182 (1925).

The spectrum of the phosphorescent flame of CS_2, as photographed by Emeléus, has been re-examined and, in addition to the characteristic flame bands constituting Emeléus's first group, it has been found that the second group includes bands of SO and CS. The SO bands were relatively much stronger than in the normal flame.

Preliminary investigations have been made of a group of bands in the ultra-violet which have been provisionally attributed to carbonyl sulphide, COS. These have not been observed in any of the experiments on flames.

A vibrational analysis of the flame bands has been found to be in general agreement with Rosen's scheme for S_2 as regards the ultra-violet bands, but to differ from it considerably for the less refrangible bands. In particular, the amended scheme introduces an additional $v'v''$ progression, which includes the strongest flame bands, and thus requires that Rosen's v' values should be increased by unity throughout.

The authors desire to express their thanks to Mr. C. V. Jackson for his valuable assistance in the preparation of carbonyl sulphide and in taking photographs with 1-metre grating.

DESCRIPTION OF PLATES.

Plate 14.

a. CS_2 flame, showing characteristic bands from blue to near ultra-violet. Fe comparison.

b. Flame in N_2O, with chimney; showing SO_2 absorption λ 3200–2800.

c. Flame in O_2, with chimney; showing SO_2 absorption λ 3200–2800.

d. Flame in air, with chimney; showing SO_2 absorption λ 3200–2800.

e. Flame in open air; feeble S_2 absorption λ 3000–2600.

f. Flame with jet of O_2, observed in direction A of fig. 1; S_2 emission from visible to ultra-violet.

g. Same as *f* but observed in direction B; S_2 *emission* from blue to near ultra-violet, S_2 *absorption* in ultra-violet.

h. Sulphur in active nitrogen; S_2 emission bands to λ 2829.

k. S_2 absorption as in *g* with greater dispersion.

Note.—*a* and *k* taken with spectrograph E2; *b*–*h* taken with spectrograph E31; *b*–*e* with Cu comparisons; *f*, *g*, *k* with Fe comparisons.

Plate 15.

a. Vacuum tube spectrum of sulphur, λ 6200–4400, 1 metre grating.

b. Vacuum tube spectrum of sulphur, λ 4800–2829; spectrograph E2.

c, *c′*. Flame and tube spectra, λ 4400–3800, showing fine structure; 1-metre grating.

d. Flame with jet of O_2, observed in direction A of fig. 1, showing S_2 *emission* bands from red to ultra-violet; spectrograph E2.

Fe arc comparisons throughout.

The Spectrum of the Hydrogen-Nitrous Oxide Flame.

By A. Fowler, D.Sc., F.R.S., Yarrow Research Professor of the Royal Society, and J. S. Badami, B.Sc., Imperial College, South Kensington.

(Received July 7, 1931.)

[Plates 10, 11.]

Introductory.

The present investigation was undertaken on the suggestion of Mr. H. T. Tizard, F.R.S., arising out of some experiments in progress at the National Physical Laboratory. Previous observations of the spectrum of the hydrogen-nitrous oxide flame have not been very complete, and it was hoped that more extended observations, in connection with our present knowledge of the constitution of the molecules associated with certain band spectra, might throw further light on the process of combustion. Observations have accordingly been made over the range λ8225 to λ2250, with the result that the spectrum in question has been found to be identical with that of the flame of ammonia burning in oxygen, apart from differences in intensities of certain bands in the two spectra.

The spectrum of the ammonia-oxygen flame has previously been described, but it may be useful to give an account of the experiments which have been made, and to state the modern interpretation of the spectra observed. As the results may be of interest to some who are not spectroscopists, it has been thought desirable to include a brief account of the spectra which form the basis of the conclusions reached.

Reference Spectra.

" *Water Vapour* " *Bands* (HO).—Emission bands attributed to water vapour were discovered simultaneously by Liveing and Dewar* and by Huggins.† Liveing and Dewar observed these bands to be well developed in the flames of hydrogen or hydrocarbons burning in oxygen, and less strongly in the flames of non-hydrogenous gases, such as carbonic oxide and cyanogen, if burnt in moist oxygen. The same bands were also observed in uncondensed discharges in vacuum tubes containing moist gases, but they disappeared when the gas and apparatus had been thoroughly dried. A more complete description was given later by the same authors.*

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* ' Proc. Roy. Soc.,' vol. 30, pp. 498 and 580 (1880).

† ' Proc. Roy. Soc.,' vol. 30, p. 576 (1880).

The spectrum consists of a number of bands degraded towards the red, of which one at λ 3064 is especially conspicuous. Other band heads are at λλ 3472, 3428, 2811 and 2608, but band lines were found by Liveing and Dewar to extend as far as λ 4100 towards the violet and to λ 2268 in the ultra-violet.

The analysis of this spectrum, in the light of the modern theory of band spectra, has resulted in its definite assignment to HO molecules.†

"*Ammonia*" *Bands.*—Three groups of bands are associated with the spectrum of ammonia. The first was observed by Schuster‡ as a broad yellowish-green band, about λ 5635, in the spectrum of a vacuum tube through which a continuous stream of ammonia gas was passed. It was noted that the band at once disappeared when the supply of ammonia was cut off. Schuster's band was subsequently found by Lecoq§ to be double, with components about λλ 5643 and 5681.

The second and most characteristic band associated with ammonia, having its strongest part about λ 3360, was first described by Eder,|| who observed it in the ammonia-oxygen flame, and designated it the β band. This band was afterwards observed by Lewis¶ in the spectra of vacuum tubes containing mixtures of hydrogen and nitrogen, and a more detailed investigation of the band, and of its occurrence in the solar spectrum, was given by Fowler and Gregory.** Lewis observed that, unlike the Schuster bands, the β band persisted after the supply of ammonia was stopped.

The third system of bands, extending over the whole of the visible spectrum, was also observed by Eder in the ammonia-oxygen flame, and was distinguished by him as the α band. As a result of an investigation of the structure and chemistry of the ammonia-oxygen flame, it was concluded by A. Reis†† that this band belonged to the spectrum of ammonia.

The α band was investigated in greater detail in Professor Fowler's laboratory by W. B. Rimmer,‡‡ who found that it could also be observed in the

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* 'Phil. Trans.,' vol. 179, p. 27 (1888).

† *Cf.* D. Jack, 'Proc. Roy. Soc.,' A, vol. 115, p. 373 (1927).

‡ 'Rep. Brit. Assoc.,' p. 38 (1872).

§ 'C. R. Acad. Sci.,' Paris, vol. 101, p. 42 (1885).

|| 'Denkschr. Wien. Akad.,' vol. 60, p. 1 (1893).

¶ 'Astrophys. J.,' vol. 40, p. 154 (1914).

** 'Phil. Trans.,' A, vol. 218, p. 351 (1919).

†† 'Z. Phys. Chem.,' vol. 76, p. 560 (1911).

‡‡ 'Proc. Roy. Soc.,' A, vol. 103, p. 696 (1923).

uncondensed discharge in vacuum tubes containing ammonia at suitable pressures. Photographs taken with high resolution showed this part of the spectrum to be of great complexity, consisting of about 3000 band lines extending from red to violet, but showing no distinct heads of bands. It was further noted by Rimmer, in agreement with Eder, that with a small supply of oxygen the α band was stronger with respect to the ultra-violet band than when the supply of oxygen was abundant.

Rimmer considered that his observations supported the suggestion of Lewis that the Schuster bands represent the true spectrum of ammonia, while the ultra-violet λ 3360 band is probably due to a more stable compound of hydrogen and nitrogen. Rimmer's investigation suggested, in addition, that the α band originates in an emission centre which represents the first stage of dissociation of the normal ammonia molecule, and that the β band represents a further stage of dissociation which precedes the final breaking up of the molecules into atoms.

Analysis of the structure of the β band, λ 3360, has been made by Hulthén and Nakamura,* from which it results that this band originates in NH molecules.

No analysis has yet been made of the α band, but Hulthén and Nakamura have expressed the opinion that this complicated system is emitted by excited NH_3 or NH_2 molecules, or a mixture of both. NH_3, however, appears to be ruled out by the experimental evidence, and if the Schuster bands have been correctly attributed to NH_3, it may provisionally be supposed that the α bands represent NH_2 molecules. It may be noted that a recent investigation by Lavin and Bates† on the gases flowing from the exit of an ammonia discharge tube have indicated the presence of an active gas, probably consisting of atomic hydrogen and NH or NH_2.

"*Third Positive Nitrogen Bands*" (NO).—Five bands in the ultra-violet, extending from λ 2718 to λ 2262, were observed by Eder in the spectrum of the ammonia-oxygen flame, and were assigned the names γ–η. These were afterwards found to be identical with the well-known double-double bands, degraded to the more refrangible side, which had been designated the "Third Positive" bands of nitrogen by Deslandres, who had shown, nevertheless, that the simultaneous presence of nitrogen and oxygen was necessary for their production. Analysis of this spectrum has resulted in its assignment to NO molecules.‡.

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* 'Nature,' vol. 119, p. 235 (1927).

† 'Proc. Nat. Acad. Sci.,' vol. 16, p. 804 (1930).

‡ R. T. Birge, 'Bull. Nat. Res. Co.,' vol. 11, No. 57, p. 69 (1926); M. Guillery, 'Z. Physik,' vol. 42, p. 121 (1927).

Previous Observations.

In connection with their experiments on the ignition points of gases, Dixon and Higgins* studied the ignition of several gases in an atmosphere of nitrous oxide. In the case of a hydrogen flame it was observed, as had previously been noted by Priestley and by Davy in the burning of a candle or taper, that an atmosphere of nitrous oxide produced a remarkable increase in the size and luminosity of the flame. The jet of unburnt gas was seen to be surrounded by a bright apricot-coloured zone, which appeared to give a continuous spectrum, while outside this was a thick sheath of a greenish-grey colour. A photograph obtained with a quartz spectrograph showed an apparently continuous spectrum from red to violet, and beyond this the ultra-violet " steam " (HO) bands.

Dixon and Higgins also recorded that when a jet of hydrogen was burnt in nitrous oxide at normal pressure in a wide glass tube, a red colouration due to the formation of nitrogen peroxide was seen stretching upwards from the level of the flame. Also, that when the hydrogen-nitrous oxide flame was divided in a Smithell's separator, no peroxide could be detected in the interconal gases, though it was formed in the outer flame. The general outcome of these experiments was to show that the ignition points of hydrogen in nitrous oxide, at corresponding pressures, were always lower than those in oxygen.

The hydrogen-nitrous oxide flame had previously been observed by S. Barratt† in connection with an investigation of the origin of cyanogen bands in the violet and ultra-violet. The presence of the β band of ammonia and the bands of water vapour was recorded, but no reference was made to the α band.

Structure of the Flames.

Mixed Jet.—In the first of the present series of experiments, nitrous oxide and hydrogen were mixed by passing the gases through the two horizontal arms of a ⊥ tube, and were then burnt at a small jet on the upright arm, as in the corresponding experiment at the National Physical Laboratory. Afterwards, it was found convenient to use a mixed-jet blowpipe, which gave a flame of the same character.

The main part of the flame was only feebly luminous, but in the lower part there was a more luminous zone which varied in appearance and brightness with varying proportions of nitrous oxide. With a supply of nitrous oxide such that a hydrogen flame about $1\frac{1}{2}$ inches in height (I*a*)* was extended to about 7 inches, the inner zone was conical in shape (I*b*), but with a suitable reduction in the supply of nitrous oxide, this inner cone was enlarged and became a semi-elliptical arch surmounted by a bright yellowish cap; the outer flame was then much reduced in length, and was of greater width (I*c*). Surrounding the inner zone there was a fairly bright yellowish-white region extending to more than half the height of the flame, and beyond this a feeble dull red portion which was of a somewhat smoky appearance.

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* 'Mem. Manchester Lit. Phil. Soc.,' vol. 71, p. 15 (1926).

† 'Proc. Roy. Soc.,' A, vol. 98, p. 44 (1920).

Two-way Blowpipe.—Experiments were also made with a two-way blowpipe in which hydrogen was passed through the outer, and nitrous oxide through the inner, tube, so that the gases were not mixed until they reached the orifice where they were burnt. In this case (I*d*) the structure of the flame was somewhat similar to that obtained with the mixed jet when there was a relatively large supply of N_2O (I*b*). The inner cone, however, was somewhat less prominent, and its upper part was surrounded by a zone of considerable brightness, as shown by the enlargement in the lower part of I*d*. No bright cap could be made to appear at the summit of the cone, and it would seem that the bright cap of I*c* was here represented by the bright zone which surrounds the inner cone.

Hydrogen Flame Surrounded by N_2O.—Further experiments were made by surrounding a flame of hydrogen with an atmosphere of nitrous oxide. This was done by enclosing the flame in a glass chimney into which nitrous oxide was passed, or by passing the hydrogen through the inner tube and nitrous oxide through the outer tube of a two-way blowpipe. Under these conditions the hydrogen flame was enlarged and much brightened, especially near the base (I*e*). No definite inner cone, however, was observed.

Spectroscopic Observations.

Mixed-jet Flame.—Visual observations of the bright cone or cap (I *b*, *c*) with a pocket spectroscope showed six fairly distinct bands, three on each side of the D lines, superposed on a continuous spectrum of moderate intensity. Photographs taken with a small quartz spectrograph (Hilger's E 31) showed these and other bands, and experiments with vacuum tubes containing compounds of nitrogen were undertaken with a view to tracing their origin. The bands were not obtained in discharges through N_2O, either alone or when mixed with hydrogen or oxygen, but were eventually found to be identical with the α bands of ammonia occurring rather feebly in tubes containing ammonia. The identification was afterwards fully confirmed by photographs of the ammonia-oxygen flame, in which the α bands are very conspicuous (II*a*). With large dispersion, as in the photographs taken by Rimmer, the bands in question become unrecognisable as such.

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* This and similar references are to the photographic reproductions, Plates 10 and 11.

It is possible that the apparent band heads, when the spectrum is viewed with small dispersion, may give a clue to the structure of this spectrum, and it may accordingly be useful to record the following roughly approximate positions :—

λ	ν	λ	ν
*6652	15,029	*5713	17,499
6470	15,452	5575	17,932
*6302	15,864	*5436	18,391
*6042	16,546	5384	18,568
5807	17,216	5265	18,988

In this table the brighter bands are marked with an asterisk.

Visual observations of the flame above the inner cone revealed no bands, but only a continuous spectrum. The outermost part of the flame was too faint for spectroscopic observation.

A photograph of the spectrum of the inner cone of the $H_2 — N_2O$ flame (I *b*), which is identical with that of the bright cap of I *c*, is reproduced in II *b*. The D lines of sodium appear near the less refrangible end, and the α bands of ammonia extend from the red side of this to the near ultra-violet. The β band at λ 3360 (NH), with the wings of band-lines on each side of the central band, is very prominent. The bands of HO are also conspicuous and in the further ultra-violet there are the double bands of NO.

The spectrum of the ammonia-oxygen flame is shown in II *a* for comparison. It will be seen that this shows the same bands as the $H_2 — N_2O$ flame, but with a somewhat different distribution of intensities. Thus, the β band being of about the same intensity in the two photographs, the HO and NO bands are decidedly stronger in the $H_2 — N_2O$ flame and the α bands of ammonia (NH_2 ?) somewhat weaker. The weak band at λ 3883 in the $H_2 — N_2O$ flame is due to "cyanogen" (CN) and was doubtless introduced by a slight impurity of a carbon compound either in the hydrogen or nitrous oxide.

The third photograph, II *c*, was taken with an image of the bright cap of the $H_2 — N_2O$ flame (I *c*) focussed on the slit of the spectrograph, and shows very clearly that while the α and β bands of ammonia and the NO bands were almost entirely restricted to the bright flame cap, the HO bands and continuous spectrum extended through the outer flame with but little diminution of intensity. Eder similarly observed that the characteristic bands of "ammonia" appeared only in the inner cone of the ammonia-oxygen flame, while the outer flame yielded the "water-vapour" bands.

Two-way Blowpipe Flame.—When the flame was produced with the two-way blowpipe, with nitrous oxide passing through the inner tube (I *d*), visual observations of the inner cone showed only a strong continuous spectrum. In the zone immediately surrounding the inner cone, however, the continuous spectrum was much weaker and the α bands were distinctly visible. Photographs also showed a continuous spectrum, and apparent discontinuities in its intensity were proved to be due to varying sensitivity of the plates, for different wave-lengths, by comparison with the spectrum of a white-light source. In the ultra-violet, the bands of HO were very strong, the NH band of moderate intensity, and the NO bands rather feeble.

The blow-through flame thus differed from the mixed-jet flame chiefly in the greater diffusion of the luminous cap of the latter, and in the increased brightness of the continuous spectrum shown by the inner cone.

Hydrogen Flame Surrounded by N_2O.—Visual observations of this flame (I*e*) showed only a bright continuous spectrum, as noted by Dixon and Higgins. Photographs of the spectrum also showed a strong continuous spectrum extending from red to violet, together with bands of HO, and sometimes traces of the NH band at λ 3360. The spectrum of the hydrogen flame was thus scarcely affected by the substitution of nitrous oxide for ordinary air outside the flame, except as regards the greatly increased intensity of the continuous spectrum.

Summary.

Observations of the bright cap or cone, which appears near the base of the hydrogen-nitrous oxide flame in a mixed jet have shown that the spectrum is closely similar to that of the ammonia-oxygen flame. Each of these flames shows bands due to the molecules NH, HO and NO, and the so-called "α bands" of ammonia, which have been provisionally attributed to NH_2 molecules on the basis of experimental evidence. The Schuster bands, probably due to NH_3 molecules, were not observed. The hydrogen-nitrous oxide flame differs from the ammonia-oxygen flame in the greater intensity of the NH and HO bands, and the lower intensity of the NH_2 ? bands, the

NH band at λ 3360 being about the same in both. The outer cones of both these flames appear to exhibit nothing but the bands of HO and a continuous spectrum

DESCRIPTION OF PLATES 10, 11.

PLATE 10.

(*a*) Hydrogen flame.

(*b*) H_2 flame with large supply of N_2O. Mixed jet.

(*c*) H_2 flame with small supply of N_2O. Mixed jet.

(*d*) H_2 flame with N_2O blown through. The lower photograph is an enlarged view of the inner cone from the same negative.

(*e*) H_2 flame surrounded by N_2O.

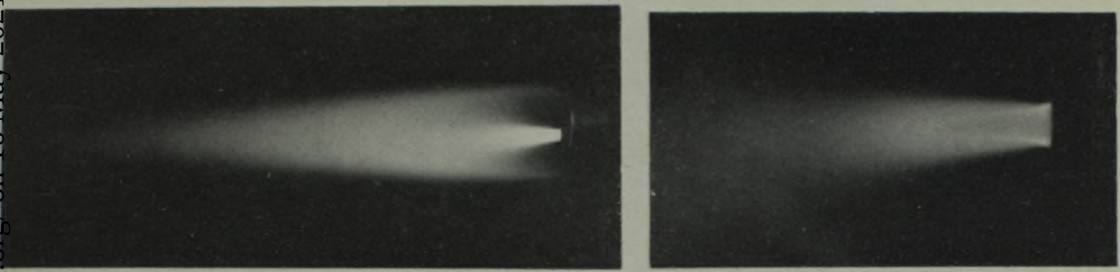
PLATE 11.

(*a*) Spectrum of ammonia-oxygen flame; oxygen passed through inner tube and ammonia through outer tube of blowpipe.

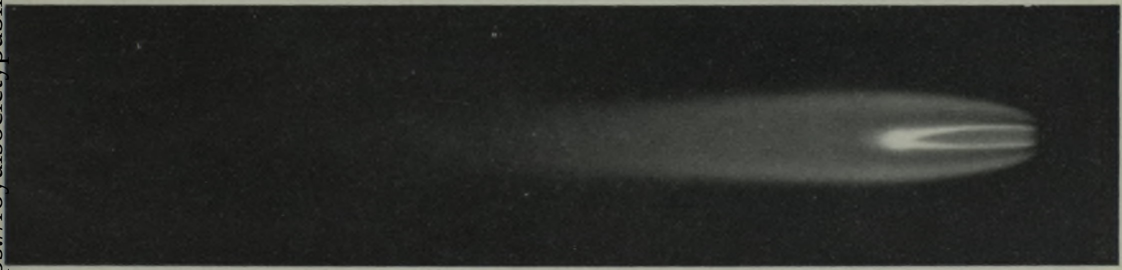
(*b*) Spectrum of H_2–N_2O flame, inner cone (I, *b*).

(*c*) Spectrum of H_2–N_2O flame, bright cap and flame above it (I, *c*). The apparent bands on the red side of the Na lines and the patch from λ 5000 to λ 4000, which extend across the spectrum, represent continuous spectrum as photographed with small dispersion on a plate of varying sensitivity. The dark lines on the upper edge of the spectrum are due to daylight which accidentally entered the slit.

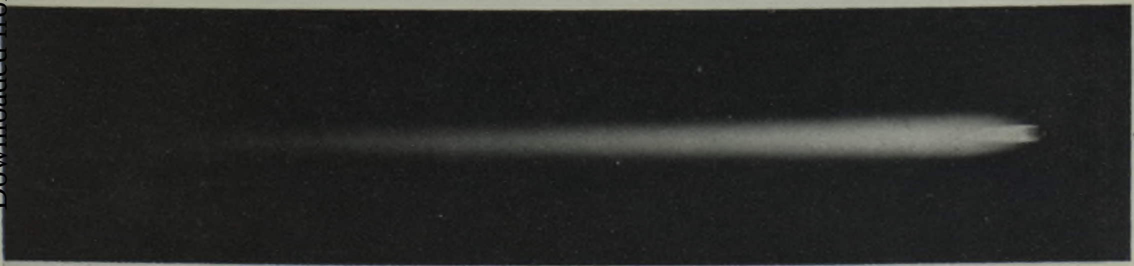
e



d

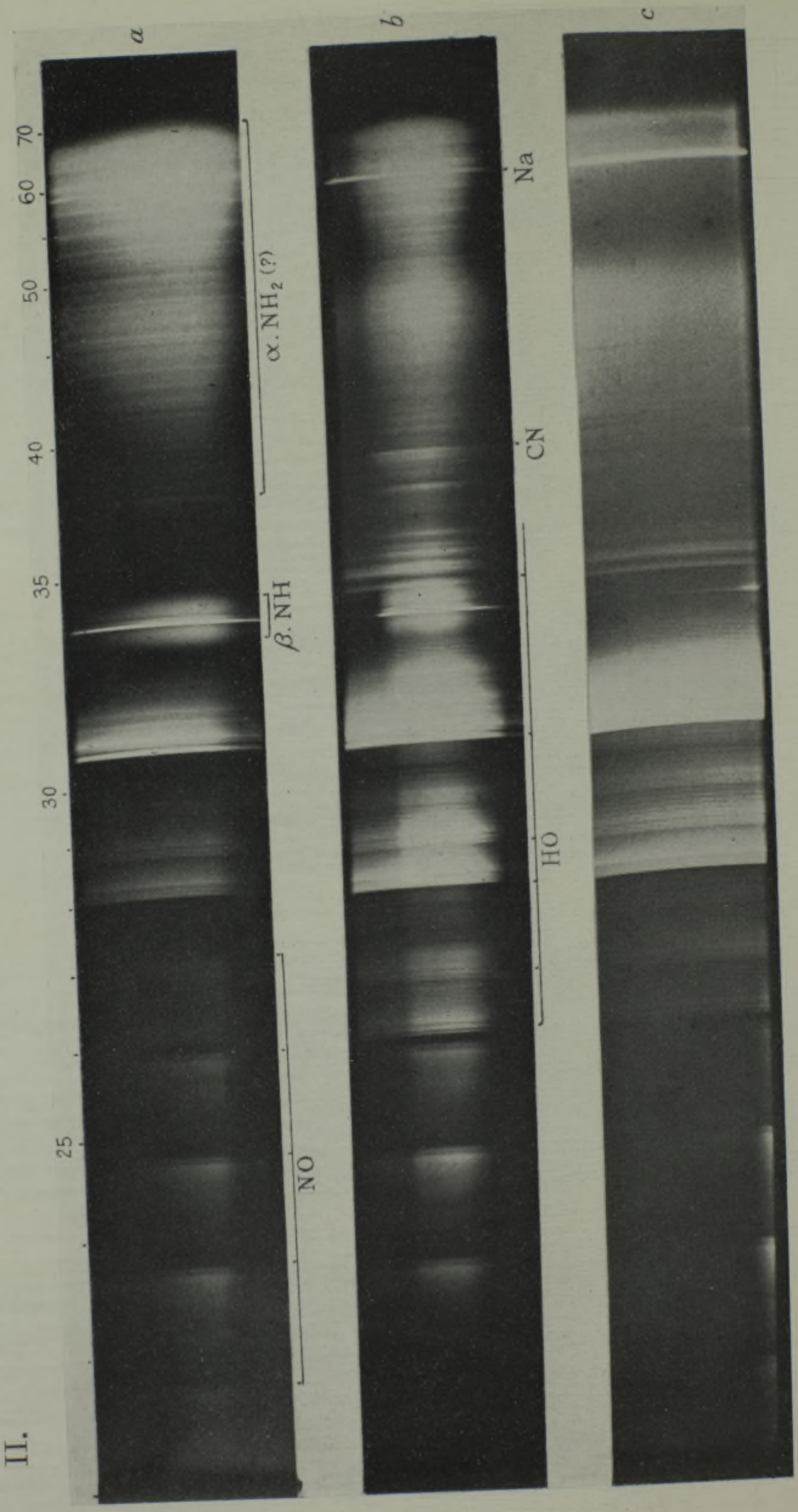


c



b

a


a
b
c
70
60
50
40
35
30
25
α. NH$_2$ (?)
β. NH
NO
Na
CN
HO
II.

The Band Spectrum of Nitrogen Sulphide (*NS*).

By A. FOWLER, D.Sc., F.R.S., Yarrow Research Professor of the Royal Society, and C. J. BAKKER, Ph.D.

(Received January 20, 1932.)

(PLATE 1.)

Introductory.

The present investigation had its origin in an observation by one of us that in a vacuum tube containing sulphur vapour with an impurity of nitrogen, there appeared a previously unrecorded band spectrum which bore a striking resemblance to that of nitric oxide (NO). As only sulphur and nitrogen were known to be present, this similarity suggested that the new spectrum might be due to nitrogen sulphide (NS), since oxygen and sulphur have the same number of valence electrons. This supposition appears to be fully confirmed by the further experiments which have been made and by the vibrational analysis of the bands. The principal members of both sets of bands occur in the ultra-violet and nearly in the same region. It will be convenient first to give a brief account of the bands of nitric oxide.

The Bands of Nitric Oxide.

The principal bands of NO are well known from their occurrence in air vacuum tubes; they were long ago named the "Third Positive Bands of Nitrogen" by Deslandres,* who, nevertheless, considered that the presence of both nitrogen and oxygen was necessary for their production. These bands were observed by Fowler and Strutt (now Lord Rayleigh)† to appear in the spectrum of the nitrogen afterglow, and the opinion was expressed that nitrogen alone was capable of producing them. Subsequent work by Lewis‡ and by Strutt,§ however, supported the view that the bands were produced only when both nitrogen and oxygen were present. During the present investigation, also, it has been found that the bands in question do not occur in vacuum tubes containing nitrogen when oxygen has been completely removed. These experimental results are in agreement with the conclusion derived from analyses of the band structure that the bands originate in the diatomic molecule NO.

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* 'C. R. Acad. Sci. Paris,' vol. 101, p. 1256 (1885).

† 'Proc. Roy. Soc.,' A, vol. 85, p. 377 (1911).

‡ 'Phil. Mag.,' vol. 25, p. 826 (1913).

§ 'Proc. Roy. Soc.,' A, vol. 93, p. 254 (1917).

The general appearance of the NO spectrum as it occurs in an air vacuum tube is illustrated in Plate 1, spectrum *b*. It will be seen that the "Third Positive" bands appear with double-double heads and are degraded towards shorter wave-lengths. These were designated the "γ bands" by Fowler and Strutt in their account of the spectrum of the nitrogen afterglow, and this designation has since been widely adopted.

Another system of bands, designated the "β bands" by Fowler and Strutt, appears rather feebly in the air vacuum tube, but becomes very prominent in the nitrogen afterglow spectrum, as shown in Plate 1, spectrum *a*. The β bands are doublets and are degraded towards the red; in the afterglow they can be traced well into the visible spectrum.*

A third system of bands of NO was first recognised by Knauss,† with active nitrogen as source, and was named by him the "δ system" of NO. These bands are degraded towards shorter wave-lengths, and are similar in appearance and separations to the γ bands. The approximate wave-lengths given by Knauss were 1913, 1987, 2062, 2142, 2229 and 2320 A. More accurate wave-lengths for three of the bands were afterwards given by R. Schmid.‡

Still another system of bands of NO, incompletely observed in absorption by Leifson§ has been designated the "ε system" by Birge.|| Leifson's wave-lengths for these are 1877·2, 1799·6, 1729·7 and 1666·6 A.

Structure of NO *spectrum.*

The orderly arrangement of the γ bands was first shown by Deslandres,¶ but has been indicated more completely by M. Guillery** in connection with her rotational analyses of some of the bands. The structure of this spectrum, however, has not yet been presented with the completeness and accuracy which is desirable.

It results from the work of Mulliken†† and others that the γ-bands represent transitions $A\,^2\Sigma \rightarrow X\,^2\Pi$ (see fig. 1), the wider separation corresponding with the two Π levels, and the narrower ones representing the heads of different branches. The (0, 0) band is at λ 2269 and appears strongly in the absorption

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* Johnson and Jenkins, 'Phil. Mag.,' vol. 2, p. 621 (1926).

† 'Phys. Rev.,' vol. 32, p. 422 (1928).

‡ 'Z. Physik,' vol. 59, p. 42 (1930).

§ 'Astrophys. J.,' vol. 63, p. 73 (1926).

|| 'Int. Crit. Tables,' vol. 5, p. 409 (1929).

¶ 'C. R. Acad. Sci. Paris,' vol. 139, p. 584 (1904).

** 'Z. Physik,' vol. 42, p. 121 (1927).

†† 'Phys. Rev.,' vol. 28, p. 493 (1926).

spectrum of NO at ordinary temperatures, together with other members of the $(v' \rightarrow 0)$ progression.

The origins of the γ-bands are represented by the following formulæ given by Schmid* :—

$$\nu_0 = 44199 + (2358\cdot0v' - 16\cdot3v'^2) - (1892\cdot12v'' - 14\cdot424v''^2),$$
$$\nu_0 = 44079 + (2358\cdot0v' - 16\cdot3v'^2) - (1891\cdot98v'' - 14\cdot454v''^2).$$

Accurate measurements and rotational analyses of several of the β bands have been made by Jenkins, Barton and Mulliken.† These bands correspond with transitions $B\,^2\Pi_{3/2} \rightarrow X\,^2\Pi_{3/2}$ and $B\,^2\Pi_{1/2} \rightarrow X\,^2\Pi_{1/2}$, and the heads are represented approximately by the following formulæ given by Johnson and Jenkins :—

$$\nu_{\text{head}} = \left.\begin{matrix}45394\cdot6\\45485\cdot0\end{matrix}\right\} + (1029v' - 7\cdot5v'^2) - (1889\cdot05v'' - 13\cdot96v''^2).$$

More accurate formulæ, involving higher powers of v' and v'' have been given by Jenkins, Barton and Mulliken. The separation $B\,^2\Pi_{3/2} - B\,^2\Pi_{1/2}$ is not observed directly, but is deduced from the observed $\Delta\nu = 124$ of the γ system and $\Delta\nu = 91$ of the β system. The (0, 0) bands of this system, the calculated positions of which are $\lambda\lambda$ 2202·2 and 2197·8, have not been observed either in absorption or in emission.

The δ system of NO is attributed to transitions from a higher $^2\Sigma$ level (c in fig. 1) to the final levels $X\,^2\Pi$, the bands having the same separations and vibrational levels as the γ system. The (0, 0) band has its least refrangible head near λ 1910 (ν 52340) and has been observed in the absorption spectrum of NO by Leifson. It has also been observed as a strong absorption band by R. Curry and J. Rankine at the Imperial College. The plates obtained by the latter observers also exhibit the $(v' \rightarrow 0)$ progression of the γ system and several members of the $(v' \rightarrow 0)$ progression in the β system, beginning with $v' = 2$.

The transitions involved in the production of the NO bands are indicated in fig. 1, which is drawn to scale with the doublet separations enlarged ten times. Corresponding transitions in NS are also shown in this diagram. The designations of the various levels for NO are in accordance with those of Mulliken‡ and Weizel.§

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* ' Z. Physik,' vol. 64, p. 84 (1930).

† ' Phys. Rev.,' vol. 30, p. 150 (1927).

‡ ' Chem. Rev.,' vol. 6, p. 524 (1929).

§ " Bandenspektren," p. 364 (Leipzig, 1931).

Production of NS *Bands.*

Compounds of nitrogen and sulphur are highly explosive, and in these preliminary experiments it was accordingly considered sufficient to produce the NS bands by passing uncondensed discharges through a mixture of nitrogen and sulphur vapour. The discharge tube was of an ordinary end-on type, made of Pyrex glass and provided with quartz windows ; the capillary had a diameter of about 2 mm. and the electrodes were of aluminium. A small well, projecting below one of the wider parts of the tube, served to contain the sulphur, and the supply could be replenished through a ground-in stopper vertically above the well. The tube was exhausted by a three-stage mercury vapour pump, backed by a Hyvac pump, a liquid air trap being interposed to prevent mercury from entering the discharge tube and to protect the pumps from sulphur.

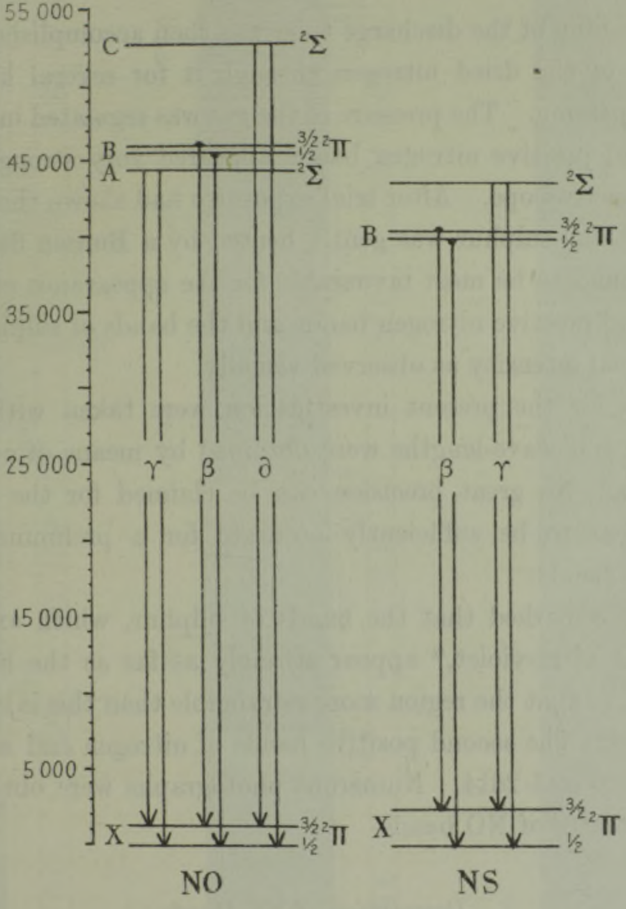

FIG. 1.

In order to obtain the NS bands in this way it is essential to "clean" the discharge tube thoroughly. The presence of even a very little oxygen, in conjunction with the nitrogen, suffices to bring out strongly the γ bands of NO, which lie in the same region of the spectrum and would obscure the bands of NS. It was found sufficient to use commercial nitrogen, dried by passage over P_2O_5.

The final cleaning of the discharge tube was then accomplished by passing a gentle stream of the dried nitrogen through it for several hours while the discharge was passing. The pressure of the gas was regulated in such a manner that the second positive nitrogen bands appeared very strongly as observed with a hand spectroscope. After trial exposures had shown the absence of the γ bands of NO, the sulphur was gently heated by a Bunsen flame. The conditions were found to be most favourable for the appearance of the NS bands when the second positive nitrogen bands and the bands of sulphur appeared to be of about equal intensity as observed visually.

Photographs for the present investigation were taken with small quartz spectrographs, and wave-lengths were obtained by means of copper arc comparison spectra. No great precision can be claimed for the measurements, but they appear to be sufficiently accurate for a preliminary vibrational analysis of the bands.

It should be remarked that the bands of sulphur, which extend from the visible into the ultra-violet,* appear strongly as far as the head at λ 2829, but no further, so that the region more refrangible than this is left clear for the spectrum of NS. The second positive bands of nitrogen end with the pair of heads at $\lambda\lambda$ 2820 and 2814. Numerous photographs were obtained in which there were no traces of NO bands.

Description of NS *Bands.*

The NS bands, as obtained in the way described above, are illustrated in Plate 1, spectrum *c*, from which it will be observed that the most prominent bands correspond closely in appearance with the γ and β bands of NO. It will accordingly be convenient to give the same names to corresponding systems in both spectra.

As in NO, the γ system presents bands with double-double heads, degraded to the violet, but the separations are greater in NS than in NO and successive bands are closer together.

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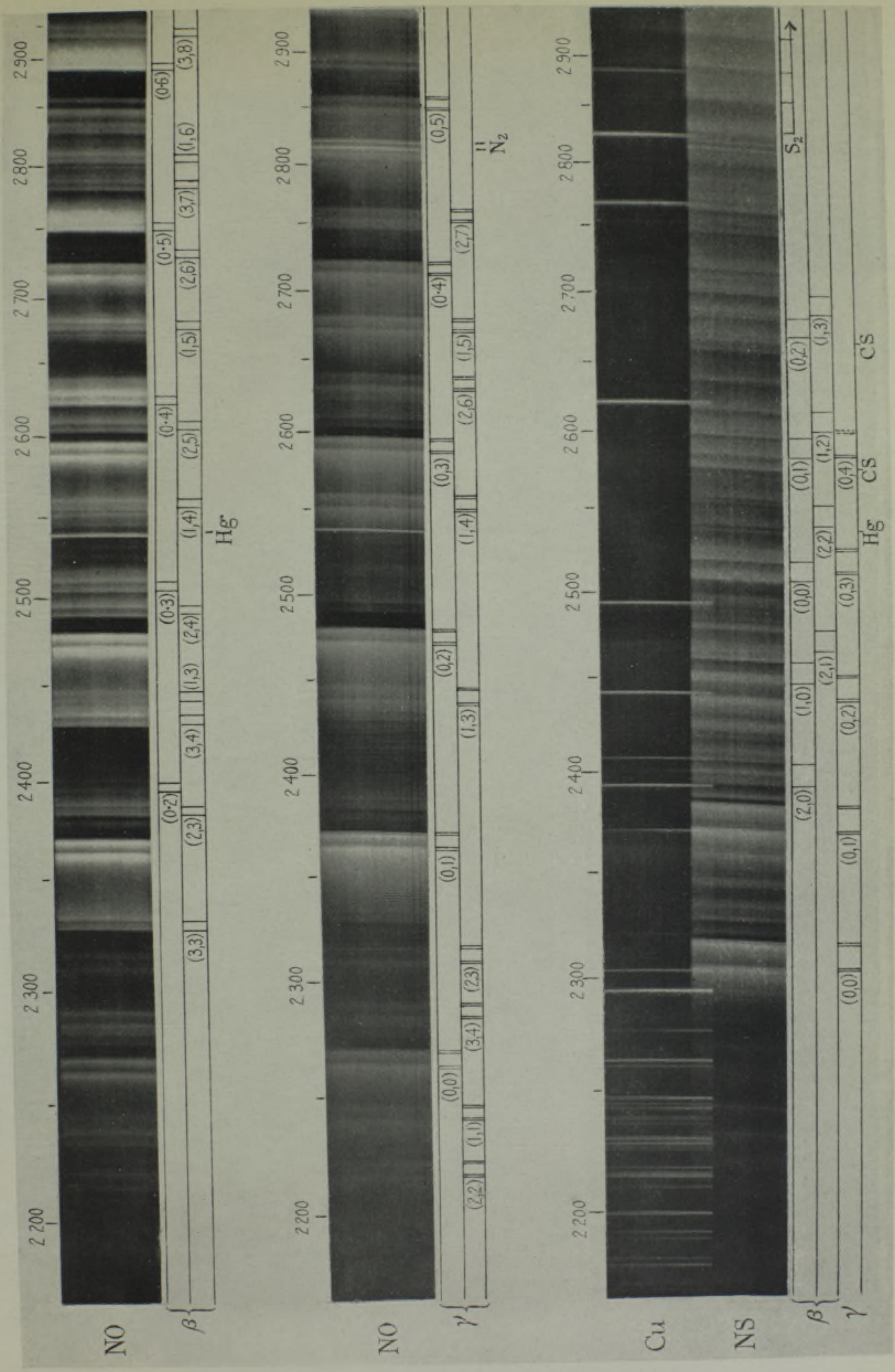
* Fowler and Vaidya, 'Proc. Roy. Soc.,' A, vol. 132, p. 310 (1931).


NO
β
NO
γ
Cu
NS
β
γ
2200
2300
2400
2500
2600
2700
2800
2900
(3,3)
(2,3)
(3,4)
(1,3)
(2,4)
(1,4)
(2,5)
(1,5)
(2,6)
(3,7)
(1,6)
(3,8)
(0·2)
(0·3)
(0·4)
(0·5)
(0·6)
Hg
(2,2)
(1,1)
(0,0)
(3,4)
(23)
(0,1)
(1,3)
(0,2)
(1,4)
(0,3)
(2,6)
(1,5)
(0·4)
(2,7)
(0,5)
N₂
(2,0)
(1,0)
(0,0)
(0,1)
(0,2)
(2,1)
(2,2)
(1,2)
(1,3)
(0,0)
(0,1)
(0,2)
(0,3)
(0,4)
Hg
CS
CS
S₂

The pairs of bands forming the β system of NS are also more widely separated than those of NO and not so far apart.

The photographs of NS show, in addition, a number of bands, degraded to the red, which do not appear to belong to the β system, and have no counterpart in NO. The strongest of these are at wave-lengths 2762·0, 2744·5, 2715·2, 2655·6, 2634·2, 2557·3, 2400·2 and 2387·3. Their intensities appear to have a constant relation to those of the β bands, but it is not yet certain that they are due to NS.

In some of the photographs, including the one reproduced, Plate 1, there are two fairly strong heads of bands, degraded to the red, at wave-lengths 2575·9 and 2662·3. These are due to carbon monosulphide, as found by a careful comparison with photographs of the spectrum of this substance taken by L. C. Martin* and with the measurements of W. Jevons.† Besides the main heads, the first of which is double, some of the adjacent heads on their less refrangible sides are also shown feebly when the principal heads are strong. Independent evidence of the presence of small impurity of carbon is afforded by the occurrence of the CN band at λ 3883.

The γ *Bands of* NS.

Details of the γ band-heads which have so far been traced are shown below :—

v'' v'	0		1		2		3		4
0	43142 (10) 43166 (10)	*1202* *1204*	41940 (10) 41962 (10)	*1187* *1189*	40753 (5) 40773 (5)	*1172* *1173*	39581 (3) 39600 (3)		
	224		*222*		*222*		*223*		
	43367 (8) 43389 (8)	*1204* *1206*	42162 (10) 42183 (10)	*1187* *1189*	40975 (4) 40994 (4)	*1171* *1170*	39804 (3) 39824 (3)	*1161* *1160*	38643 (1) 38664 (1)

The numbers in parentheses, to the right of the wave-numbers, represent estimated intensities.

The vibrational quantum numbers have been assigned by analogy with the γ system of NO. In NO the (0, 0) band at λ 2269 is clearly indicated as such by the absorption spectrum, and by the fact that it is the obvious termination of the $(0 \rightarrow v'')$ progression. There is no evidence at present from the absorption spectrum in the case of NS, but since the photographs extend far enough to have exhibited an additional band if it had been present, the bright band of which the first head is at ν 43142 may reasonably be taken to be the (0, 0) band.

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* 'Proc. Roy. Soc.,' A, vol. 89, p. 127 (1913).

† 'Proc. Roy. Soc.,' A, vol. 117, p. 351 (1928).

There are some indications of faint bands which may represent the $(1 \rightarrow v'')$ progression, but further work is necessary to establish them with certainty.

The above heads are represented approximately by the following formulæ :—

$$^2\Sigma \rightarrow X\,^2\Pi_{3/2}: \ \nu_{\text{head}} = \left.\begin{matrix}43142\\43166\end{matrix}\right\} - (1212v'' - 8v''^2)$$

$$^2\Sigma \rightarrow X\,^2\Pi_{1/2}: \ \nu_{\text{head}} = \left.\begin{matrix}43367\\43389\end{matrix}\right\} - (1212v'' - 8v''^2).$$

As will appear from what follows, the $^2\Sigma$ level lies above B $^2\Pi$ in NS, and it is not certain with which of the two $^2\Sigma$ levels in NO it corresponds.

The β *Bands of* NS.

The β system of NS has been more completely observed than the γ system. Since both have the same final levels, the assignment of vibrational quantum numbers follows simply from the Δν of the γ system. All the bands which have been identified are included in the following scheme :—

v'' v'	0		1		2		3
0	39694 (8)	*1202*	38493 (6)	*1191*	37302 (4)		
	186		*183*		*183*		
	39880 (8)	*1204*	38676 (5)	*1191*	37485 (3)		
	933				*933*		
	945				*947*		
1	40627 (7)	*1203*	+	*1189*	38235 (4)	*1173*	37062 (5)
	198				*197*		*194*
	40825 (6)	*1203*	+	*1190*	38432 (3)	*1176*	37256 (4)
	922				*921*		
	925				*924*		
2	41549 (4)	*1203*	40346 (3)	*1190*	39156 (3)		
	201		*200*		*201*		
	41750 (4)	*1204*	40546 (3)	*1189*	39357 (2)		

These band heads may be approximately represented by the following formulæ :—

$$\text{B}\,^2\Pi_{3/2} \rightarrow \text{X}\,^2\Pi_{3/2}: \ \nu_{\text{head}} = 39694 + (938\cdot5v' - 5\cdot5v'^2) - (1212\cdot25v'' - 7\cdot75v''^2)$$

$$\text{B}\,^2\Pi_{1/2} \rightarrow \text{X}\,^2\Pi_{1/2}: \ \nu_{\text{head}} = 39880 + (956\cdot5v' - 10\cdot5v'^2) - (1212\cdot25v'' - 7\cdot75v''^2).$$

As in NO, the separation of the B $^2\Pi$ levels is the difference between the separation of the X $^2\Pi$ levels and the observed separations of the β bands ; that is, for NS, approximately 224 — 186 = 38.

If the quantum numbers have been correctly assigned, the β system of NS differs from that of NO in the occurrence of the (0, 0) and other bands of low quantum numbers which have not been observed in NO. The intensity distribution in NS thus appears to be quite different from that in NO. Johnson and Jenkins's Table III (*loc. cit.*) indicates a wide-open Condon parabola for NO, with its maximum at about $v'' = 8$, whilst in NS the parabola appears to be a rather narrow one having its axis roughly in the direction of the diagonal. The difference in intensity distribution, however, is in general accordance with expectation, since in NO the ratio of w''_e to w'_e is about 1·9, whilst in NS it is about 1·25.

The (1, 1) band of NS appears to be entirely absent.

Classified Bands of NS.

λ (intensity).	γ bands ($v'v''$).	β bands ($v'v''$).
2697·40 (5)	—	37062 (1, 3)
2683·35 (4)	—	37256 (1, 3)
2680·05 (4)	—	37302 (0, 2)
2667·00 (3)	—	37485 (0, 2)
2614·60 (4)	—	38235 (1, 2)
2601·25 (3)	—	38432 (1, 2)
2597·15 (6)	—	38493 (0, 1)
2587·00 (1)	38643 (0, 4)	—
2585·60 (1)	38664	
2584·80 (5)	—	38676 (0, 1)
2553·10 (3)	—	39156 (2, 2)
2540·10 (2)	—	39357 (2, 2)
2525·70 (3)	39581 (0, 3)	—
2524·50 (3)	39600	
2518·50 (8)	—	39694 (0, 0)
2511·55 (3)	39804 (0, 3)	—
2510·30 (3)	39824	
2506·75 (8)	—	39880 (0, 0)
2477·80 (3)	—	40346 (2, 1)
2465·60 (3)	—	40546 (2, 1)
2460·70 (7)	—	40627 (1, 0)
2453·05 (5)	40753 (0, 2)	—
2451·85 (5)	40773	
2448·75 (6)	—	40825 (1, 0)
2439·75 (4)	40975 (0, 2)	—
2438·65 (4)	40994	
2406·05 (4)	—	41549 (2, 0)
2394·45 (4)	—	41750 (2, 0)
2383·63 (10)	41940 (0, 1)	—
2382·40 (10)	41962	
2371·10 (10)	42162 (0, 1)	—
2369·90 (10)	42183	
2317·19 (10)	43142 (0, 0)	—
2315·94 (10)	43166	
2305·17 (8)	43367 (0, 0)	—
2304·03 (8)	43389	

Summary.

A spectrum of bands attributed to nitrogen sulphide (NS) has been obtained by passing uncondensed discharges through tubes containing nitrogen and sulphur vapour. The spectrum is strikingly similar to that of nitric oxide (NO) and appears in nearly the same (ultra-violet) region. Two systems of bands, corresponding with the well-known γ and β bands of NO, are clearly shown. In NS the doublet separations are larger, and the separations of successive bands smaller, than in NO.

DESCRIPTION OF PLATE.

a.—**Nitrogen afterglow, showing γ and β bands of NO strongly.** (For 0·2 ... *read* 0, 2 ...)

b.—**Air vacuum tube; γ bands strong, β bands weak.**

c.—**Vacuum tube containing nitrogen and sulphur vapour.** (The bands at λ 2576 and λ 2662 are due to an impurity of CS.) Copper arc comparison.

Notes on the Theory of Radiation.

By C. G. Darwin, F.R.S.

(Received January 22, 1932.)

It will probably be agreed that among all the recent developments of the quantum theory, one of the least satisfactory is the theory of radiation. The present paper is intended as a preliminary to a new line of attack on the subject. It was begun some time ago, but owing to lack of success in carrying it to a conclusion, its publication has been much delayed. In the meantime other papers have appeared,* which in some respects follow the same train of thought. The authors of these works have carried their methods further in some directions than I have attempted, but there is still perhaps room for the discussion of a number of questions from the rather different point of view adopted here.

1. The main principle of the present work is the idea that, since matter and light both possess the dual characters of particle and wave, a similar mathematical treatment ought to be applied to both, and that this has not yet been

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* Landau and Peierls, 'Z. Physik,' vol. 62, p. 188 (1930); Oppenheimer, 'Phys. Rev.,' vol. 38, p. 725 (1931).

Spectrum of the Afterglow of Carbon Dioxide.

By A. Fowler, D.Sc., F.R.S., Yarrow Research Professor, and A. G. Gaydon, B.Sc., Research Student, Imperial College.

(Received July 15, 1933.)

[Plate 4.]

Introductory.

When compounds of carbon and oxygen are excited to luminosity in vacuum tubes, they give rise to a large number of band systems, depending upon the conditions of electrical discharge. Most of these systems have been discussed by various authors, and on the basis of the theory of band spectra have been attributed to transitions between different states of the molecule CO. Details of these systems, including those ascribed to the ionized molecule CO^+, have been conveniently summarized by Jevons* and by Kayser and Konen.†

Another band system (Deslandres' second negative) which occurs under favourable conditions has been attributed by Bair,‡ and by Fox, Duffendack and Barker§ to the triatomic molecule CO_2, since the bands appear most strongly in CO_2, and are especially developed when a stream of this gas is passing through the discharge tube. The suggested CO_2 origin of these bands appears to be supported by Smyth's partial analysis of their structure.||

Quite recently, still another set of bands has been observed by Mlle. Marie Kaczyńska¶ in the spectrum of the afterglow of the discharge through CO_2. The observations were made by drawing gas from the discharge tube into a side tube, as in the well-known similar procedure for observations of the afterglow of nitrogen. The afterglow was stated to be blue-grey in colour and to be most persistent at a pressure of about 2 mm. of mercury. As the pressure was increased, the intensity of the luminescence was increased and the colour became blue, but its extent and duration diminished rapidly. Increased intensity was also obtained by frequent renewals of the gas in the discharge tube. With an alternating current of 60 mA., the luminescence was observed

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* 'Report on Band Spectra of Diatomic Molecules,' p. 286, The Physical Society (1932).

† "Handbuch der Spectroscopie," vol. 8, p. 302 (1932).

‡ 'Astrophys. J.,' vol. 52, p. 312 (1920).

§ 'Proc. Nat. Acad. Sci.,' vol. 13, p. 302 (1927).

|| 'Phys. Rev.,' vol. 38, p. 2000 (1931).

¶ 'Bull. Int. Acad. Polonaises,' A, vol. 1A, p. 16 (1931).

to a distance of about 40 cm. and its duration was 8 seconds. The brightest part of the spectrum of the afterglow was found to extend from λ 3850 to λ 4836, and to be quite free from the Ångström bands of CO, which were the most prominent feature in the spectrum of the exciting discharge. No further details of the spectrum, however, were given.

The present investigation of the spectrum of the CO_2 afterglow was undertaken in connection with work in progress on the spectrum of the flame of carbon monoxide. This flame spectrum has been found to have nothing in common with the spectra of oxides of carbon which have been observed in vacuum tubes, and it seemed possible that a further investigation of the CO_2 afterglow might aid in its interpretation. It has been found, in fact, that apart from slight differences in relative intensities, the bands of the CO flame spectrum are identical with those of the CO_2 afterglow, at least in the region λ 3500 to λ 4850. As observed in the flame with considerable dispersion, the spectrum is extremely complex and the constitution of the emitting molecule cannot yet be certainly stated. The general experimental evidence, however, is in favour of the supposition that the bands of the afterglow and of the CO flame originate in molecules of CO_2.

Experimental.

Attempts to observe the afterglow by drawing gas from the discharge tube into a side tube did not give very satisfactory results, and another device (due to A. G. G.) was adopted. The main feature of this was the use of a mercury break with a shutter adapted so as to cut off the light from the spectrograph when the discharge was passing and to allow it to pass in the intervals between the discharges when the afterglow was visible. The mercury break was of the usual form, driven by an electric motor, but some of the plates were removed so that contact was made and broken only twice in each complete revolution. A rectangular flap of brass, blackened so as not to reflect light, was secured to the vertical spindle of the break and was adjusted between the discharge tube and the slit of the spectrograph so as to permit no light from the direct discharge to pass.

An 18-inch induction coil was used, and it was found necessary to introduce a fairly long spark gap in series with the discharge tube. The adjustment of the gap in order to obtain the best results was somewhat critical, but with due care the arrangement was found to work quite satisfactorily.

The discharge tube used in these experiments was 50 cm. in length and 7 mm.

in internal diameter, and of the form shown at T in fig. 1. To facilitate collimation, the main part of the tube was mounted with its axis vertical, and the upper end was closed with a quartz window, G. The electrodes consisted of stout aluminium rods, FF, with a suitable clearance between them and the walls of the tube. Of the many discharge tubes which were tried, those of about the dimensions stated were found to give the most satisfactory results. The discharge tube, and the side tube, A, for preparing the gas, were made of pyrex glass, while the remainder of the system was of ordinary glass, joints being made with red sealing wax where necessary. No rubber tube was used, except in the short lead to the pump.

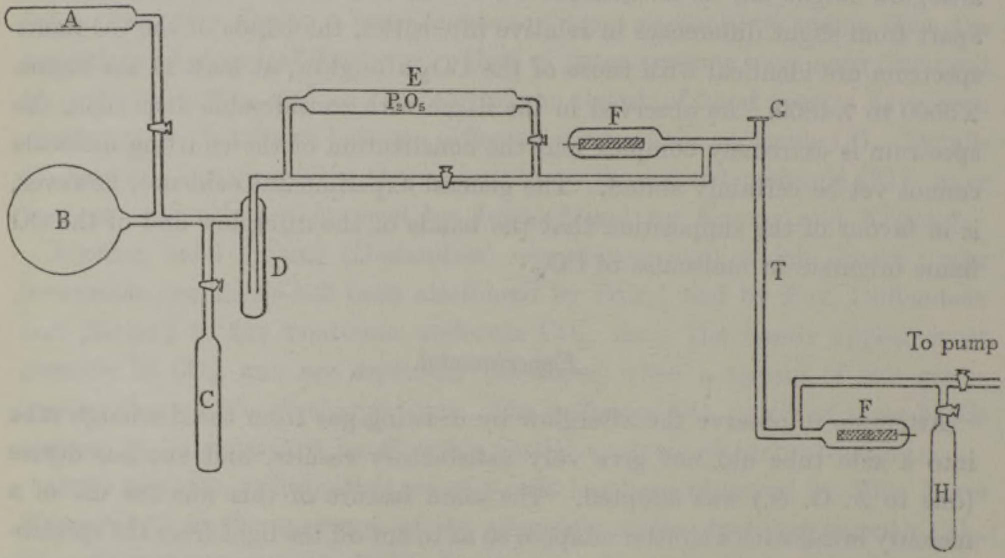


FIG. 1.

The carbon dioxide was prepared by heating magnesium carbonate in the side tube, A, and was stored in the litre flask, B. The gas was condensed in the side tube, C, by freezing with liquid air, and it was then possible to pump out any air or other impurity liberated by the heating of the tube A for the preparation of CO_2. On removing the liquid air from the trap, C, the carbon dioxide volatilized first, leaving most of the water vapour in C, which was closed as soon as sufficient gas had entered the storage flask, B. The trap shown at D was further introduced to remove water vapour by applying either solid carbon dioxide or a mixture of alcohol and liquid air. After leaving the reservoir, B, the gas passed through a phosphorus pentoxide drying tube, E, into the discharge tube. The whole system was first evacuated by a good mechanical pump, giving a pressure estimated at 0·001 mm., and a charcoal-liquid air trap, H, was used further to improve the vacuum.

Light from the discharge tube passing through the window, G, was reflected by a small speculum mirror through a right angle, to render the beam of light horizontal and in coincidence with the collimator of the spectrograph. A quartz lens placed near the mirror formed an image of the discharge on the rotating shutter, and a second quartz lens focussed the light from this image on the slit of the spectrograph. Care was taken that full illumination of the collimating lens was secured.

Occurrence of the Afterglow.

The afterglow, as noted by Mlle. Kaczyńska, was observed to be of a bluish-grey colour, but it was always very feeble, so that long exposures were necessary for photographs of the spectrum. Under favourable conditions, it was observed to persist for about two seconds when the experiment was made in a darkened room. A powerful discharge was found to be necessary for its production. Experiments with a condensed discharge, however, were not very successful on account of the intense heating of the discharge tube; the afterglow was still present, but was less blue in colour, and the spectrum was the same as that obtained when the uncondensed discharge was used.

The afterglow was better observed the more completely the CO_2 was dried, but although the "water vapour" bands at λ 3064 did not appear in the spectrum of the discharge itself, they were always present in that of the afterglow.

As possibly having some bearing upon the interpretation of the afterglow and its spectrum, observations were also made with the same apparatus when CO was substituted for CO_2 in the discharge tube, the CO being prepared by dropping formic acid into pure sulphuric acid. In the first experiments, a very feeble afterglow was observed but this disappeared completely when water vapour was removed by the use of the liquid air trap D, (fig. 1). Under these conditions, with the gas at various pressures, exposures of 10 hours duration, using a small spectrograph and a wide slit, yielded no trace of an afterglow spectrum. The admission of a trace of water vapour, however, caused the reappearance of a feeble afterglow, and this was again extinguished when a larger quantity of water vapour was introduced. A photograph obtained when the afterglow was present, though rather weak, was sufficient to show that the spectrum was the same as that obtained when the gas in the discharge tube was CO_2. No afterglow at all was observed when water vapour alone was passed through the discharge tube.

Spectrum of the Exciting Discharge.

A photograph of the spectrum of the discharge which appeared to be most effective in generating the afterglow is reproduced, together with that of the afterglow, in Plate 4, Nos. 1 and 2. The main features of the spectrum of the discharge are the Ångström bands of CO and the so-called "Third Positive" bands of this gas, all of which are of great intensity. Bands which have been attributed to CO_2, among which are bands degraded towards the red, having their heads at λλ 3247, 3370 and 3503, were entirely absent. In the further ultra-violet the bands appearing in the discharge tube (out of range in Plate 4) were those of the "Fourth Positive" system of CO. The bands of Deslandres' "First Negative" group, which require much greater energy for their production, and are now attributed to CO^+, were entirely absent.

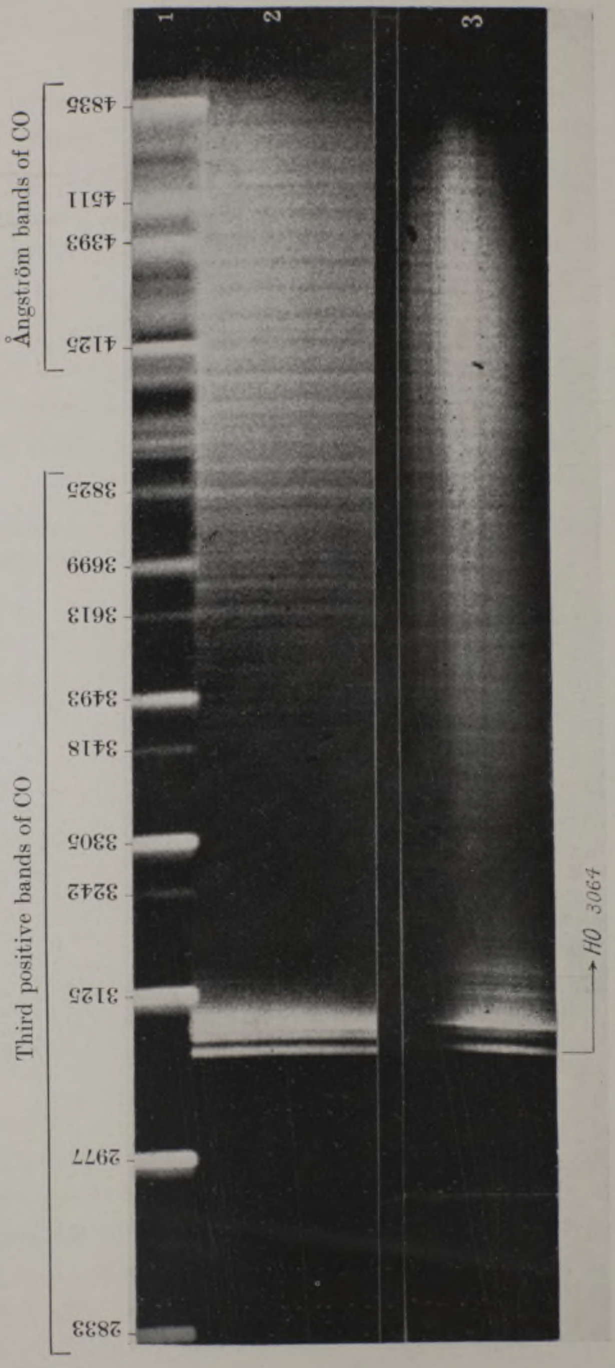
It should be noted further that the spectrum of the discharge gave no indications of either molecular or atomic carbon, and no evidence of the presence of atomic oxygen. Since the CO shown in the spectrum of the discharge tube has been derived from CO_2, oxygen must also have been present, and in view of the absence of the well-known bands due to ionized oxygen molecules ($O_2{}^+$), it must be concluded that the oxygen liberated under the conditions of the present experiments was in the form of neutral oxygen molecules. The most characteristic bands of such molecules, however, have been observed only in absorption, and no direct confirmation of their presence was given by the spectra obtained.

The phenomena observed in the afterglow would accordingly appear to depend upon the interaction between neutral oxygen molecules and excited neutral molecules of carbon monoxide.

Spectrum of the Afterglow.

On account of the feeble luminosity of the afterglow, photographs of the spectrum could be obtained only with instruments of small dispersion. Several photographs were taken with a Hilger small quartz spectrograph (E3) and others with a large-aperture glass spectrograph giving about 2½ times the dispersion in the blue and nearly twice the rapidity.

The character of the spectrum, as depicted with small dispersion, will be gathered from Plate 4, No. 2. In agreement with Mlle. Kaczyńska, it appears


1
2
3
4835
4511
4393
4125
Ångström bands of CO
3825
3699
3613
3493
3418
3305
3242
3125
2977
2833
Third positive bands of CO
HO 3064

(*Facing p.* 367.)

quite conclusively that the spectrum of the afterglow has nothing in common with that of the exciting discharge. The spectrum consists of a succession of narrow bands of various intensities, following each other at short intervals, and the bands are not clearly degraded either towards the red or the ultra-violet. The bands could not be identified with any of the numerous band systems of CO or with the known bands of CO_2, but, in due course, it was recognized that the spectrum was closely similar to that of the flame of CO burning in air or oxygen. The similarity of the two spectra will be gathered from the comparison of spectra Nos. 2 and 3 in Plate 4. There are slight differences in the relative intensities of some of the bands, and in contrast with the CO flame the afterglow is comparatively free from continuous spectrum, so that the characteristic bands are more clearly displayed. On account of the much greater brightness of the flame, the true character of the spectrum can at present be more completely investigated by observations of the flame than of the feeble afterglow.

Numerous experiments have been made with vacuum tube discharges of various forms in the hope of obtaining a brighter source of the afterglow bands, but so far they have not been successful.

Spectrum of the Flame of CO.

An extended series of observations of the flame spectrum of CO under varied conditions was made in Professor Bone's laboratory a few years ago by Weston.* His papers on the subject included a description of the spectrum by one of the present authors (A. F.) and approximate measures of 52 of the principal bands in the region λ 3911 to λ 5555. These measures were made on a plate taken with a Hilger E2 quartz spectrograph, and in view of the ill-defined character of the bands they were believed to be subject to errors amounting to at least 2 or 3 Ångströms. It was concluded that "the CO flame bands constitute a characteristic spectrum which is quite distinct from the more familiar oxy-carbon bands which have been observed in vacuum tubes."

Among numerous other results, it was found by Weston that when the gas was burnt in air at reduced pressure, the banded part of the spectrum became more distinct, while the continuous part became less intense. By the kind permission of Professor Bone, one of the photographs taken under these conditions (No. 15 on Plate 1 of Weston's first paper) is reproduced in No. 3, Plate 4, for comparison with the afterglow spectrum, No. 2; this represents the flame of CO burning in oxygen at a pressure of 100 mm. In this photograph the bands occupy precisely the same positions as those of CO burning in air at ordinary pressure, and a careful comparison has shown that they are also in complete agreement with the bands of the afterglow.

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* 'Proc. Roy. Soc.,' A, vol. 109, pp. 176, 523 (1925).

An important observation made by Weston was that when the CO was well dried, the water vapour bands, which are prominent when the undried gas is burnt, were almost absent from the spectrum, while the continuous and banded parts of the spectrum were apparently unchanged. The characteristic features of the flame spectrum thus appeared to be independent of the presence or absence of water vapour.

The conclusion reached by Weston, with the support of Professor Bone, was that " in the flame of pure (undried) carbon monoxide, two sets of independent interactions occur simultaneously, namely, (*a*) direct interactions between carbon monoxide and oxygen, exciting radiations which give rise to the continuous and banded parts of the spectrum, and to the characteristic blue colour of the flame, and (*b*) interactions between CO and OH_2 molecules, which originate the ' steam lines ' in the spectrum." There was, however, no evidence at that time to show whether it was molecular or atomic oxygen that was concerned in the interaction of carbon monoxide with oxygen.

The spectrum of the CO flame has also been investigated by Kondratjev* over the region λ 2800 to λ 5000. In these experiments, a mixture of CO and O_2 in combining proportions was passed through a quartz tube which was heated in an electric furnace to temperatures of 600°–750° C., the pressure of the mixed gases ranging from 20 mm. to 60 mm. From the reproduction of the spectrum and the tabulated wave-lengths of the bands measured, it seems clear that the spectrum obtained in this way did not differ materially from that of the CO flame in air or oxygen. Kondratjev gave several reasons for attributing the characteristic bands to CO_2, but did not consider that this conclusion was finally established.

The afterglow spectrum, as photographed with small dispersion, has an appearance of simplicity which is not maintained when its analogue in the CO flame spectrum is photographed with the larger dispersion of Hilger's quartz spectrographs E2 and E1. With these instruments the spectrum has been found to be extremely complicated, consisting of a great number of narrow bands of various intensities, many of them being double. A few bands are possibly shaded to the red, but the majority of them are not clearly degraded in either direction. Some progress has been made in the analysis of the structure of the spectrum, but the results are still far from complete. The complicated system of bands, however, strongly suggests that the origin of the spectrum is something more complex than a diatomic molecule.

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* ' Z. Physik,' vol. 63, p. 322 (1930).

Summary and Conclusions.

The more important results of the experiments which have been mentioned above may conveniently be summarized as follows :—

(1) The spectrum of the afterglow of CO_2 is different from any known spectrum given by oxides of carbon in vacuum tubes, but has been found to resemble that given by the flame of CO burning in air or oxygen.

(2) The spectrum of the exciting discharge indicates that the afterglow is generated by the interaction of excited neutral molecules of CO with neutral molecules of oxygen. Under the conditions which gave rise to the afterglow, there was no evidence of dissociation of the CO_2 other than into neutral molecules of CO and O_2.

(3) The characteristic bands of the CO flame spectrum are independent of the presence of water vapour in the CO undergoing combustion (Weston).

(4) The HO bands which occurred in the spectrum of the afterglow probably originated in interactions between excited CO or O_2 molecules and water vapour which was present in quantities too small to reveal its presence in the exciting discharge.

These observations appear to be entirely in favour of the view that the bands of the CO_2 afterglow, and of the CO flame, are produced by the direct combination of CO and O_2, without dissociation into atoms of carbon and oxygen or molecules of carbon.

The probability that the characteristic bands of the afterglow represent CO_2 molecules is also strongly suggested by the great complexity which is revealed by the use of spectrographs of adequate resolving power.

DESCRIPTION OF PLATE.

Fig. 1.—Spectrum of CO_2 discharge by which the afterglow shown in No. 2 was generated. Exposure 6 seconds. The Ångström and Third Positive bands of CO are very conspicuous. The Fourth Positive CO bands were also present but are out of range in the reproduction.

Fig. 2.—Spectrum of the CO_2 afterglow. Exposure 12 hours.

Fig. 3.—Spectrum of the flame of CO burning in oxygen at a pressure of 100 mm. (Weston).

(2) The effect of surface on the reaction has been studied.

(3) The length of the induction period has been observed to pass through a maximum with increasing pressure of nitrogen peroxide.

(4) A reaction mechanism has been suggested. Oxygen atoms arising from the nitrogen peroxide are assumed to start chains in which CH_2 radicals and oxygen atoms are concerned. These ultimately lead to explosion of the gases when a limiting velocity involving self-heating of the mixture is reached. The theory is in agreement both with the kinetic results of the present paper and with the analytical data of Bone and others relative to the products of explosion and slow reaction.

Band Spectrum of Aluminium Chloride (AlCl).

By B. N. Bhaduri, M.Sc., Research Student, Imperial College, South Kensington, and A. Fowler, F.R.S., Yarrow Research Professor of the Royal Society.

(Received February 17, 1934.)

[Plate 8.]

Introductory.

In the course of experiments on the spectrum of hydrogen chloride, a strong band system having its greatest intensity about λ 2610 was observed when using discharge tubes with aluminium electrodes. It was found that these bands had previously been noted by Jevons* as occurring in his experiments on silicon chloride in active nitrogen, and had subsequently been described and attributed by him† to aluminium chloride. The photographs obtained by the authors, however, showed this band system in far greater detail than those of Jevons, and as it obviously included a large number of bands associated with the heavier isotope of chlorine, it seemed desirable to investigate the structure of the spectrum more completely.

For the more complete production of this band system, Jevons passed discharges through the vapour of aluminium chloride, $AlCl_3$, and this method has been adopted in the present investigation. As obtained in this way, the band system extends from λ 2555 to about λ 2810 and exhibits features of considerable interest besides those due to the presence of isotopes.

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* 'Proc. Roy. Soc.,' A, vol. 89, p. 187 (1913).

† 'Proc. Roy. Soc.,' A, vol. 106, p. 186 (1924).

The experiments made by Jevons left no doubt that the bands under consideration originated in molecules containing aluminium and chlorine. Thus, the bands were not detected in the spectra of discharges between aluminium electrodes in gases other than chlorine, nor in chlorine between electrodes of gold. The vibrational analysis included in the present paper further demonstrates conclusively that the bands are due to diatomic molecules AlCl.

Experimental.

The discharge tube employed was of ordinary H form, having a capillary about 1 mm. in diameter; it was made of pyrex glass and was provided with a quartz window to permit observations in the ultra-violet. The electrodes were of aluminium. A side tube contained the (solid) aluminium chloride $AlCl_3$, and a liquid air trap and a tube containing caustic soda were introduced to prevent chlorine reaching the pump.

After the exhaustion of air, the discharge tube was readily filled with the vapour $AlCl_3$ by gently heating the container with a Bunsen flame. On the displacement of air by the vapour, the colour of the discharge became pale blue, and there was no difficulty in maintaining a fairly constant pressure by continuous pumping and appropriate heating of the chloride. The vapour was pumped away from the window end of the discharge tube so as to minimize the solid deposit on the window itself.

The discharge was supplied by a Ferranti transformer, the primary being at 80 volts and taking a current of 3 amperes. An uncondensed discharge was used throughout. The discharge tube was thoroughly "cleaned" by pumping and heating before taking photographs, and the spectra were remarkably free from lines or bands due to impurities.

After a few preliminary photographs had been taken with smaller instruments, Hilger's E1 quartz spectrograph was used exclusively. With this instrument the dispersion ranges from 4 A. per millimetre at λ 2810 to 3 A. per millimetre at λ 2600, and the definition and resolution were very satisfactory. Exposures varied from 5 minutes for the brightest region about λ 2610 up to 3 hours for the fainter bands on both sides of this. Ilford ordinary plates were used.

The iron arc was used for reference spectra, standard wave-lengths being taken, so far as possible, from the tables published by the International Astronomical Union.* When these were inadequate in number for satisfactory

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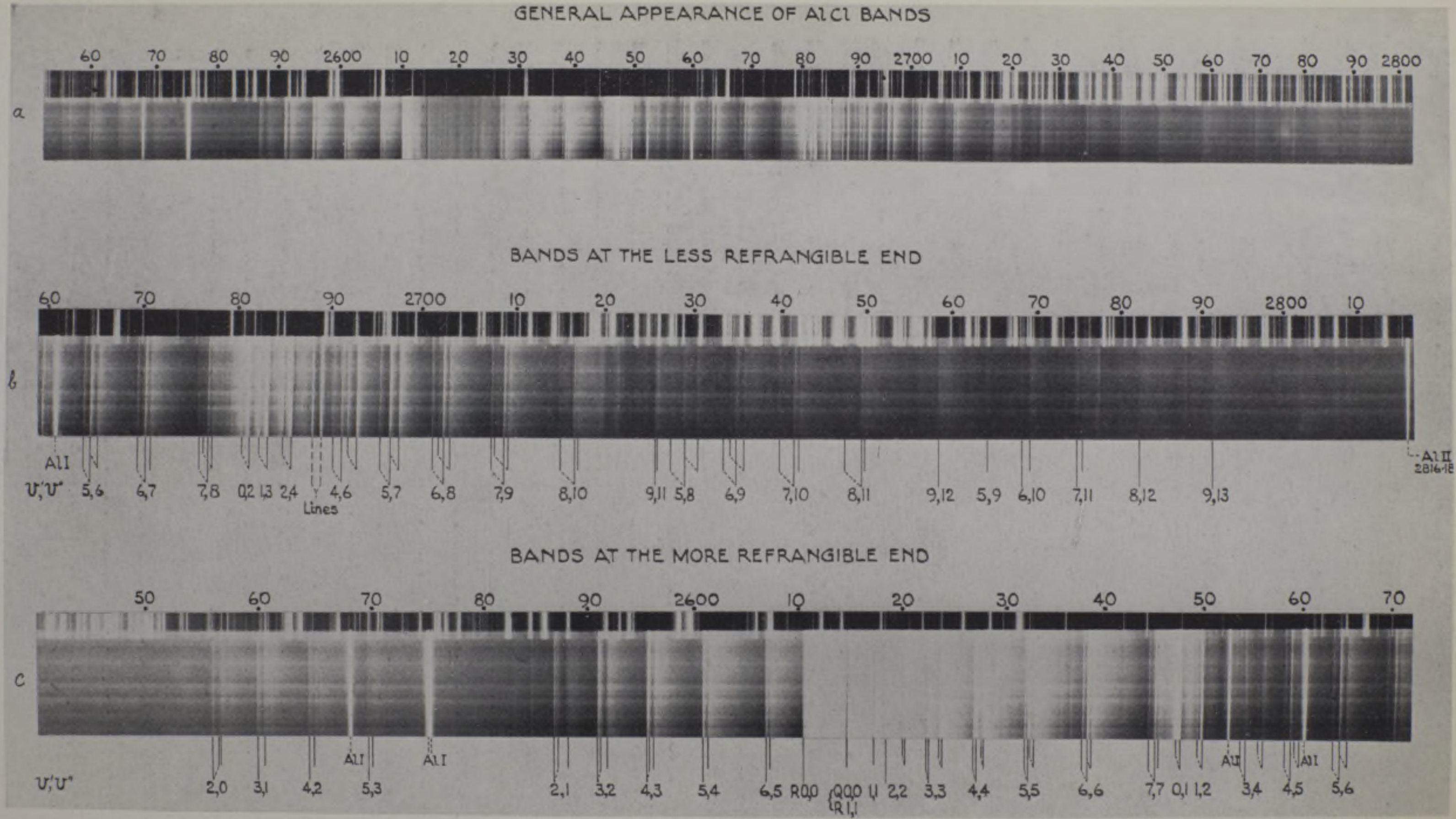
* 'Trans. Int. Astr. Union,' vol. 4 (1933).



a.—General appearance of AlCl bands, λ 2810–λ 2555. *b.*—AlCl bands towards the less refrangible side, λ 2810–λ 2660. *c.*—AlCl bands towards the more refrangible side, λ 2670–λ 2555. Long and short vertical lines represent R and Q heads respectively, the associated heads due to the less abundant isotope are represented by shorter lines and are connected together by dotted lines.

interpolations, they were supplemented by interferometer values for the vacuum iron arc given by Burns and Walters.*

Although the dispersion and resolution on the photographs may have appeared sufficient to justify an attempt to determine wave-lengths approximately correct to the third decimal place, it has not been considered desirable to express the wave-lengths to more than two decimal places. Experience has shown, in fact, that when the plate is at a large angle to the spectrum, as in a quartz spectrograph, small errors are liable to be introduced by the lack of perfect flatness of the plates. Further, there is usually some uncertainty as to correct settings on the heads of bands, and different observers might get slightly differing wave-lengths. The results of the vibrational analysis, however, indicate that the wave-lengths are mostly correct to within two or three hundredths of an angstrom.

Description of the Spectrum.

The spectrum cannot be adequately described without reference to photographs, some of which are reproduced in Plate 8. Spectrum *a* gives a general view of the whole system of bands, with the exception of a few faint bands towards the red limit, which have been omitted in order to permit the representation of the spectrum on a somewhat larger scale. Spectra *b* and *c* show different regions on a still larger scale.

It will be seen that the great majority of the bands are shaded towards the red and are spaced with obvious regularity. There are, however, two strong short sequences of bands which are shaded in the opposite direction, the least refrangible heads being at λ 2685·68 and λ 2649·73 respectively. The heads of most of the bands are very sharply defined, but the rotational structure is too fine for resolution except in a few bands, and especially in those which appear on the more refrangible side of the strong group at λ 2610, where the dispersion is greatest.

The principal band heads occur in pairs and are due to the more abundant molecules $AlCl^{35}$. These, when bright enough, are duplicated by fainter pairs which represent the less abundant molecules $AlCl^{37}$. As will appear later, the origin of the band system is near λ 2613·4, on the red side of the great band head at λ 2610, and the heavier isotope bands are displaced from the brighter bands due to $AlCl^{35}$ by amounts which are roughly proportional to the respective distances of the various bands from the origin of the system.

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* 'Pub. Allegheny Obs.,' vol. 8, No. 4 (1931).

Thus, on the red side of the origin, the displacements are towards the extreme ultra-violet and range from 32 units of wave number at λ 2810 to less than one unit at the λ 2617 band, which is near the system origin. On the other hand, on the more refrangible side of the origin, the bands due to the heavier molecules are displaced towards the red, the displacement amounting to 9 wave number units at λ 2555 where the last band is observed. These features will readily be noted on examination of the photographs, and they are indicated quantitatively in the tables which follow.

The general appearance of the double-headed bands at once suggests that the (usually) stronger components represent R branches, whilst the fainter ones, which have equally sharp heads, represent Q branches. P branches, which do not ordinarily form sharp heads (in bands shaded to the red) may be superposed on the Q branches, but this cannot be determined for want of adequate resolution of the rotational structure. For the purposes of the present paper it will suffice to designate the probably combined P and Q branches as Q. In general the R bands extend only a short distance from their heads and show no signs of structure with the dispersion employed, whilst the Q bands extend further and are in places partially resolved.

The appearance of the spectrum in the main group is considerably modified in some of the photographs on account of absorption by the luminous vapour which occupied the space between the end of the capillary of the discharge tube and the quartz window through which the spectrum was observed. Some of the band heads were definitely reversed. In the present paper, however, an attempt has been made to eliminate these absorption effects, so that the data presented refer exclusively to the spectrum of emission bands. The peculiarities of the absorption effects will form the subject of a further investigation.

Another modification of the main group of bands was found when the intensity of the discharge was considerably reduced. In particular, the head at λ 2610 then became very feeble, as in one of the photographs reproduced by Jevons. This is the R 0, 0 band and its head is at a considerable distance from the band origin; it may therefore be supposed that with low excitation the rotation band lines do not extend sufficiently far from the band origin to reach the head with any great intensity. In bands further removed from the system origin the heads are nearer to their respective band origins and appear fully developed.

In addition to the system of bands which has been described, Jevons observed eight bands, also degraded towards the red, in the region λ 3596 to λ 3111. The heads were widely separated and were of sufficiently open structure to

Table I.—Vibrational Analysis of AlCl Bands.

v' \ v''		0		1		2		3		4		5		6		7		8		9		10		11		12		13
0	Q	38237·7 (4)	477·4	37760·3 (6)†	473·2	37287·1 (4)†																						
	Q^i	—		37766·2 (3)†		37298·3 (2)†																						
	R	38299·5 (5)		—		—																						
	R^i	—		—		—																						
		QQ 439·9		440·2		441·4																						
		RR 403·4																										
1	Q	38677·6 (0)	477·1	38200·5 (4)	472·0	37728·5 (4)†	469·4	37259·1 (6)†																				
	Q^i	—		—		37734·6 (2)†		37272·1 (3)†																				
	R	38702·9 (0)	465·8	*38237·7 (4)		—																						
	R^i	38697·5 (0)		—		—																						
		QQ 430·0		429·6		428·4																						
		RR 417·3		410·3																								
2	Q	39107·6 (0)	477·5	38630·1 (1)	473·2	38156·9 (4)				37223·5 (6)†																		
	Q^i	39098·6 (0)		—		38158·2 (2)		—		37235·4 (3)†																		
	R	39120·2 (1)	472·8	38647·4 (2)	464·7	38182·7 (3)				—																		
	R^i	39110·8 (0)		38643·6 (1)		—				—																		
		QQ		418·3		417·2				415·5																		
		RR		409·5		403·7																						
3	Q			39048·4 (1)	474·3	38574·1 (2)	469·0	38105·1 (5)	466·1	37639·0 (1)																		
	Q^i			39039·4 (0)		—		38107·0 (2)		37647·2 (0)																		
	R			39056·9 (1)	470·5	38586·4 (2)	464·8	38121·6 (4)	456·8	37664·8 (1)																		
	R^i			39048·4 (0)		38583·3 (1)		38124·0 (2)		37672·3 (0)																		
						404·2		403·6		404·0																		
						399·4		396·3		390·1																		
4	Q					38978·3 (1)	469·6	38508·7 (3)	465·7	38043·0 (4)	461·1	37581·9 (1)	456·8	37125·1 (5)														
	Q^i					38970·6 (0)		—		38046·9 (1)		37590·4 (0)		37138·9 (2)														
	R					38985·8 (1)	467·9	38517·9 (2)	463·0	38054·9 (3)	456·8	37598·1 (2)	449·9	37148·2 (2)														
	R^i					38978·3 (0)		38516·4 (1)		38058·7 (2)		37606·7 (1)		37161·9 (1)														
								389·9		390·2		389·2		389·5														
								386·6		385·3		381·8		377·1														
5	Q							38898·6 (0)	465·4	38433·2 (3)	462·1	37971·1 (3)	456·5	37514·6 (2)	453·3	37061·3 (3)	449·9	36611·4 (1)	445·4	36166·0 (1)	440·3	35725·7 (0)						
	Q^i							38892·8 (0)		—		37976·0 (0)		37525·3 (1)		37075·6 (1)		36631·6 (1)		36190·5 (0)		—						
	R							38904·5 (1)	464·3	38440·2 (3)	460·3	37979·9 (3)	454·6	37525·3 (1)	449·7	37075·6 (2)	444·0	36631·6 (0)	441·1	36190·5 (0)		—						
	R^i							38898·6 (0)		—		37985·1 (1)		37535·5 (0)		37090·5 (1)		36651·8 (0)		—		—						
										—		374·8		373·7		374·2		374·4		374·0		373·5						
										372·0		371·6		369·5		367·4		363·5		361·5								
6	Q									—		38345·9 (1)	457·6	37888·3 (2)	452·8	37435·5 (2)	449·7	36985·8 (2)	445·8	36540·0 (1)	440·8	36099·2 (1)	438·3	35660·9 (0)				
	Q^i									—		—		37894·8 (1)		—		37002·8 (1)		36561·0 (1)		36124·0 (0)		—				
	R									38812·2 (0)	460·7	38351·5 (2)	456·7	37894·8 (2)	451·8	37443·0 (2)	447·9	36995·1 (3)	443·1	36552·0 (1)	437·6	36114·4 (0)	439·8	35674·2 (0)				
	R^i									—		—		37902·1 (1)		37454·7 (1)		37011·8 (1)		36573·3 (0)		36140·4 (00)		35706·3 (00)				
																356·9		356·7		357·5		356·1		356·2				
																354·1		353·1		351·7		348·7		352·8				
7	Q															37792·4 (1)	449·9	37342·5 (0)	445·0	36897·5 (2)	442·2	36455·3 (1)	438·2	36017·1 (1)	434·9	35582·2 (0)		
	Q^i															—		37356·3 (0)		36917·1 (0)		—		36045·9 (0)		35613·8 (0)		
	R															37797·1 (2)	448·9	37348·2 (2)	444·5	36903·7 (2)	440·6	36463·1 (1)	436·1	36027·0 (1)	431·3	35595·7 (0)		
	R^i															37807·1 (1)		37362·3 (1)		36922·7 (1)		36486·9 (0)		36055·4 (0)		35628·5 (00)		
																				334·7		337·8		338·1		338·4		
																				335·3		335·0		333·2		331·7		
8	Q																			37232·2 (1)	439·1	36793·1 (1)	437·9	36355·2 (0)	434·6	35920·6 (0)		
	Q^i																			—		—		—		—		
	R																			37239·0 (1)	440·9	36798·1 (1)	437·9	36360·2 (1)	432·8	35927·4 (1)		
	R^i																			—		36819·9 (0)		36387·0 (0)		35957·9 (0)		
																								316·9		316·9		
																								315·0		313·6		
9	Q																							36672·1 (1)	434·6	36237·5 (0)	430·7	35806·8 (0)
	Q^i																							—		—		—
	R																							36675·2 (1)	434·2	36241·0 (1)	429·8	35811·2 (0)
	R^i																							—		36269·7 (0)		35842·8 (0)
v' / v''																		8		9		10		11		12		13

* Falls on Q 0, 0.

† Bands degraded away from red.

(To face p. 325).

be partially resolved even with very small dispersion. These bands, however, were not observed in the present experiments, and as they have no apparent relation to the AlCl bands, they may possibly have originated in some impurity.

Vibrational Analysis.

Most of the bands were easily arranged in a v' v'' scheme representing transitions between initial vibrational levels v' and final levels v''. Consideration of intensities suggested that the most refrangible head in the main group at λ 2610·23 was to be taken as R 0, 0, whilst a band at λ 2614·44 was Q 0, 0. This assignment of the vibrational quantum numbers was subsequently confirmed by the close agreement between the calculated and observed magnitudes of the isotope displacements when the origin of the system had been determined.

The distribution of the band heads is exhibited in the usual manner in Table I. The bands are there arranged in groups such that a complete group includes the main R and Q heads and the associated isotope heads R^i and Q^i, in the order Q, Q^i, R and R^i. Some of the groups are incomplete on account of the low intensity of one or more members, and others because of their proximity to the system origin and the consequent very small displacements of the isotope heads.

The differences $\nu_{v'} - \nu_{v'-1}$, and $\nu_{v''} - \nu_{v''+1}$, are shown in Table I for both R and Q heads. It will be seen that the differences for the Q heads are very uniform in the same vertical column or horizontal row, proving that the measured positions of the Q heads are very close to the respective band origins. The corresponding differences for the R heads, as was to be expected, show no such uniformity, on account of the varying distances of the R heads from their band origins; the variations, however, are quite systematic.

Assuming then that the Q heads represent band origins, the origin of the system can be calculated in the usual way by adjusting the observed wave numbers of these heads to the well-known general formula*

$$\nu_0 = \nu_e + [\omega'_e (v' + \tfrac{1}{2}) - x'_e\, \omega'_e (v' + \tfrac{1}{2})^2 + y'_e\, \omega'_e (v' + \tfrac{1}{2})^3] - [\omega''_e (v'' + \tfrac{1}{2}) - x''_e\, \omega''_e (v'' + \tfrac{1}{2})^2],$$

where ν_0 represents band origins and ν_e the origin of the system. A cubic term is quite unnecessary for the final levels (v'') in AlCl, as clearly appears from the uniformity of the second differences between successive Q bands.

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* See Jevons' "Report on the Spectra of Diatomic Molecules," 'Phys. Soc.,' p. 56 (1932).

The mean value of the second differences is 3·9 units of wave number, and the half of this, 1·95, has been adopted for the coefficient $x''_e\,\omega''_e$. With this value, the bands 2, 0 and 2, 2 gave ω''_e as 481·20, while 9, 11 and 9, 13 gave 481·40; taking the mean of these, 481·30 was adopted for ω''_e.

Next, by a graphical extrapolation of the main sequence (0, 0; 1, 1; etc.) the origin of the system, ν_e, was found to be very near to ν 38254. With this and the constants ω''_e and $x''_e\,\omega''_e$ already determined, values of ω'_e, $x'_e\,\omega'_e$ and $y'_e\,\omega'_e$ were calculated from the three Q heads 0, 0; 5, 6; and 9, 12. The resulting equation for the Q heads of the whole system was thus found to be:

$$\nu_0 = 38254\cdot0 + [449\cdot96\,(v' + \tfrac{1}{2}) - 4\cdot37\,(v' + \tfrac{1}{2})^2 - 0\cdot216\,(v' + \tfrac{1}{2})^3] \\ - [481\cdot30\,(v'' + \tfrac{1}{2}) - 1\cdot95\,(v'' + \tfrac{1}{2})^2].$$

With these values of the constants, the agreement between the calculated and observed wave numbers of the Q heads is as close as can be expected and the sums of the positive and negative residuals are so nearly equal as to justify the retention of 38254·0 for the system origin.

Table II.—Observed-Computed Wave numbers of Q Heads.

v' \ v''	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0	0·0*	0·0	+0·3											
1	−0·6	−0·3	+1·2	+1·4										
2	−0·4*	−0·6	−0·3*		+1·7									
3		−0·1	−1·1	−0·3	−0·7									
4			−1·0	−1·0	−1·0	−0·3	+0·8							
5				−1·4	−1·1	−1·4	0·0*	+0·7	+0·9	−1·3	+3·7			
6						−0·9	−0·6	+0·6	+1·0	−1·6	+2·9	+3·0		
7								+0·5	+0·7	−1·1	+2·0	+2·2	+1·8	
8											+1·3	+1·8	+1·7	
9												−0·1*	−0·2*	−0·3*

* Used in calculation of constants.

It is of some interest to note the extent to which such an equation is capable of representing the band origins in an extended system. The observed *minus* calculated values for the Q heads are accordingly collected in Table II, where the bands used in the calculation of constants are marked with an asterisk.

The deviations from the formula are due in part to errors of observation, but it will be noted they are mostly of a systematic character and thus indicate the general accuracy of the observational data. There is, however, a marked discontinuity of the residuals at $v'' = 9$ which suggests a small perturbation of this level. For the 47 heads the mean deviation, regardless of sign is $+ 1 \cdot 1$ while the algebraical mean is $+ 0 \cdot 1$, and it is clear that the formula is sufficiently exact for the calculation of isotope displacements.

Bands Degraded away from the Red.

An unusual result of the vibrational analysis is that the strong bands degraded away from the red, which have previously been mentioned, find places in the v' v'' scheme for Q bands which are shaded towards the red. These also are accompanied by isotope bands which are displaced from the main bands by amounts in close agreement with those calculated on the supposition that they belong to the system having its origin at ν 38254. In Table III the observational data are compared with the values calculated from the general formula and from the formula for isotope displacements which is given later.

Table III.—Bands Degraded away from the Red.

v' v''.	λ (Int.).	ν obs.	ν calc.	Isotope displacement.	
				Observed.	Calculated.
Q 2, 4	2685·68 (6)	37223·5	37221·8	11·9	12·1
Q^i 2, 4	2684·82 (3)	37235·4	—		
Q 1, 3	2683·11 (6)	37259·1	37257·7	11·8	11·6
Q^i 1, 3	2682·26 (3)*	37270·9	—		
Q 0, 2	2681·10 (4)	37287·1	37286·8	11·2	11·3
Q^i 0, 2	2680·29 (2)	37298·3	—		
Q 1, 2	2649·73 (4)	37728·5	37727·3	6·1	6·2
Q^i 1, 2	2649·30 (2)	37734·6	—		
Q 0, 1	2647·50 (6)	37760·3	37760·3	5·9	5·6
Q^i 0, 1	2647·08 (3)	37766·2	—		

* There is a line or bandhead at λ 2682·19 (ν = 37272·1) which is too strong to represent the isotope alone; the presence of this makes the observation of the true isotope difficult.

The differences between the calculated and observed positions of the bands may be attributed to imperfections of the formula as well as to errors of observation, and the agreements, both for positions and isotope displacements are too close to be accidental. It must be concluded that the bands degrading away from the red form part of the system which is mainly composed of bands degraded in the opposite direction.

It may be remarked that this feature is not quite identical with, for example, the occurrence in the CN spectrum of bands degraded to the red (the so-called "tail-bands" of CN) in the same parts of the spectrum as the chief bands which degrade away from the red. The possibility of this juxtapostion arises from the relatively small difference between the coefficients x'_e ω'_e and x''_e ω''_e, so that high quantum numbers yield bands which appear in the same regions as those having smaller ones. In the present spectrum, this difference is also small, but the peculiar bands occur with *low* quantum numbers and have correspondingly great intensities.

As may be seen from Table I, the wave numbers along the sequences of the peculiar bands decrease in passing to the higher quantum numbers in a manner ordinarily regarded as appropriate for bands degraded towards the red, and thus provide an exception to the general rule.

Separation of Q and R Heads.

The spectrum of AlCl brings out very clearly some of the properties of band spectra, and for this reason it will be useful to collect the wave number differences between the Q and R heads in a form that will indicate the systematic character of the variations. This is done in Table IV.

Table IV.—Separations of R and Q Heads.

v' \ v''	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0	61·8													
1	25·3	37·2												
2	12·6	17·3	25·8											
3		8·5	12·3	16·5	25·8									
4			7·5	9·2	11·9	16·2	23·1							
5				5·9	7·0	8·8	10·7	14·3	20·2					
6						5·6	6·5	7·5	9·3	12·0	15·2			
7								4·3	5·7	6·2	7·8	9·9	13·5	
8											5·0	5·0	5·5	
9												3·1	3·5	4·4

It will be observed that the RQ separations are comparatively large in the neighbourhood of the system origin and become small with the higher quantum numbers. The variations, however, are clearly systematic.

The Isotope Bands.

As already indicated, many bands due to the molecules AlCl^{37} are very clearly developed in association with the corresponding bands of the more abundant molecules $AlCl^{35}$. Their wave numbers are included in the vibrational analysis, Table I, and in the general list of bands, Table VI.

It is of interest to compare the observed displacements of the bands of the heavier molecule with those calculated from theory. The isotopic displacement of a band $v'\ v''$ is given by the relation*

$$\nu^i_{v'v''} - \nu_{v'v''} = (\rho-1)\,(\nu_{v'v''} - \nu_e) - (\rho-1)\,[x'_e\omega'_e\,(v'+\tfrac{1}{2})^2 - x''_e\omega''_e\,(v''+\tfrac{1}{2})^2]$$
$$- 2\,(\rho-1)\,[y'_e\,\omega'_e\,(v'+\tfrac{1}{2})^3 - y''_e\omega''_e\,(v''+\tfrac{1}{2})^3],$$

where ν^i refers to the isotope and the various coefficients have the values already shown in the equation for the whole system of bands. The constant ρ is given by

$$\rho = \sqrt{\frac{\mu}{\mu^i}}$$

where μ and μ^i are the "reduced" or "effective" masses of the two molecules which are involved. If M_1 and M_2 be the masses of the two atoms in a molecule

$$\mu = \frac{M_1M_2}{M_1 + M_2}\,.$$

For AlCl we have the masses:

$$Cl^{35} = 34{\cdot}983\,;\quad Cl^{37} = 36{\cdot}980\,;\quad \text{and}\quad Al = 26{\cdot}97,$$

on the scale of $O = 16$, and with the result that $\rho = 0{\cdot}98818$; or $(\rho - 1) = -\,0{\cdot}01182$.

With this value of $(\rho - 1)$ the isotope displacements in AlCl are given by the equation

$$\nu^i_{v'v''} - \nu_{v'v''} = (\rho-1)\,(\nu_{v'v''} - 38254{\cdot}0) - (\rho-1)\,[4{\cdot}37\,(v'+\tfrac{1}{2})^2 - 1{\cdot}45\,(v''+\tfrac{1}{2})^2]$$
$$- 2\,(\rho-1)\,[0{\cdot}216\,(v'+\tfrac{1}{2})^3].$$

The displacement is towards higher or lower wave numbers according as $(\nu^i - \nu)$ is positive or negative. The band due to the heavier molecule is always displaced from that of the lighter one in the direction of the system origin.

The observational data are collected in Table V, and the calculated values are enclosed in brackets for comparison.

The calculated values shown in Table V are vibrational displacements. Strictly, these should be corrected for rotational displacement for proper comparison with the observed values. The Q heads, being at or close to the band origins, are unaffected by the rotational effect, but the R^i heads are

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* "Jevons' Report," p. 213.

Table V.—Isotope Displacements.

v' \ v''	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0	— (0·2)	5·9Q (5·8)	11·2Q (11·3)											
1	−5·4R (−4·9)		6·1Q (6·2)	11·8Q (11·6)										
2	−9·2 (−9·7)	−3·8R (−4·1)	1·3Q (1·4)	—	11·9Q (12·1)									
3		−8·8 (−8·6)	−3·1R (−3·1)	2·1 (2·3)	7·9 (7·6)									
4			−7·6 (−7·1)	−1·5R (−1·8)	3·8 (3·5)	8·6 (8·8)	13·8 (13·9)							
5				−5·8 (−5·6)		5·1 (5·1)	10·4 (10·2)	14·6 (15·2)	20·2 (20·2)	24·5Q (25·0)				
6							6·0 (6·9)	11·7R (11·9)	16·9 (16·8)	21·2 (21·8)	25·4 (26·6)	32·1R (31·2)		
7								10·0R (9·2)	13·9 (14·2)	19·3 (19·0)	23·8R (23·8)	28·6 (28·4)	32·2 (33·0)	
8											21·8R (21·6)	26·8R (26·2)	30·5R (30·9)	
9													28·7R (29·3)	31·6R (33·8)

displaced towards the origins of the respective bands by amounts nearly proportional to their distances from their origins. The amount of displacement is given approximately by $2(\rho - 1) \times (R - Q)$.* For the AlCl bands, the displacement is approximately one-fortieth of the R — Q separations shown in Table IV. For bands on the less refrangible side of the system origin, the corrections are to be subtracted from the calculated vibrational displacements and added numerically for bands on the more refrangible side. As will be seen from Table IV, these corrections will not exceed 0·6 of a unit of wave number, except for the 0, 0 and 1, 1 bands in which the displacements are too small for measurement. This corresponds to about 0·04 A. and is probably not appreciably greater than the errors of measurement of the distances between $AlCl^{35}$ and $AlCl^{37}$ heads. Thus the observed isotope separations for the R heads may be compared with the calculated vibrational displacements without serious error.

The observed separations entered in Table V are the means of measured intervals Q^iQ, R^iR when both have been observed; when only one has been measured the tabulated $\Delta\nu$ is followed by the letter Q or R as the case may be.

It will be seen that the agreement between the calculated and observed displacements is very close for nearly all the bands. The difference exceeds one unit in only two of the bands, namely, R 6, 10 and R 9, 13 each of which is difficult to measure on account of low intensities. The mean difference between the observed and calculated values taken without regard to sign is 0·5 unit of wave number.

Distribution of Intensities.

The intensities of the bandheads have been estimated visually on a scale ranging from 6 for the strongest bands to 0 and 00 for the weakest. In fig. 1 these visual estimates are arranged in a $v'v''$ scheme, with intensities substituted for wave numbers, and it will be seen that the locus of the stronger bands is in accordance with Condon's theoretical interpretation. As expected from the theory, since ω'_e and ω''_e are not very different, the parabola is a narrow one, as for the yellow bands of SrF and the green bands of BaF, the values of ω'_e and ω''_e being nearly the same for all the three spectra. The 0, 0 band is found to lie near the vertex of the curve and in following the sequence to higher values of v', v'' the intensity is found to fall off in a regular manner.

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* See "Jevons' Report," p. 216, for exact formula.

Usually there are two intensity maxima separated by a minimum in accordance with the prediction of the theory that there are in general two preferred vibrational levels v'' in the final electronic state for a given vibrational level v' in the initial electronic state.

Intensity distribution of Q Band-heads.

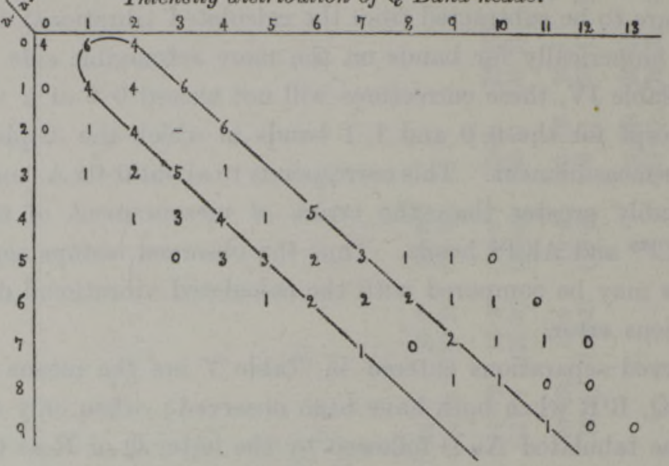

FIG. 1.

In general, the estimates of the relative intensities of the heads representing the more and less abundant molecules, AlCl³⁵ and AlCl³⁷, are in accordance with the known ratio of the abundance of the chlorine isotopes (3 : 1). In a few bands the estimates were difficult on account of their superposition on the shading of other bands.

Classified Bands.

The band heads which have been classified are collected in order of wave-length in Table VI, and most of them will be readily identified in the photographs reproduced in Plate 8.

Table VI.—Classified Bands.

λλ (Intensity).	νν.	Classification.	λλ (Intensity).	νν.	Classification.
2809·57 (0)	35582·2	Q 7, 12	2782·57 (1)	35927·4	R 8, 12
08·50 (0)	595·7	R 7, 12	80·21 (0)	957·9	R*i* 8, 12
07·08 (0)	613·8	Q*i* 7, 12	75·64 (1)	36017·1	Q 7, 11
05·92 (00)	628·5	R*i* 7, 12	74·88 (1)	027·0	R 7, 11
03·37 (0)	660·9	Q 6, 11	73·42 (0)	045·9	Q*i* 7, 11
02·32 (0)	674·2	R 6, 11	72·69 (0)	055·4	R*i* 7, 11
2799·80 (00)	706·3	R*i* 6, 11	69·33 (1)	099·2	Q 6, 10
98·28 (0)	725·7	Q 5, 10	68·16 (0)	114·4	R 6, 10
91·94 (0)	806·8	Q 9, 13	67·43 (0)	124·0	Q*i* 6, 10
91·60 (0)	811·2	R 9, 13	66·17 (00)	140·4	R*i* 6, 10
89·14 (0)	842·8	R*i* 9, 13	64·21 (1)	166·0	Q 5, 9
83·10 (0)	920·6	Q 8, 12	62·34 (0)	190·5	R, Q*i* 5, 9

Table VI—(continued).

λλ (Intensity).	νν.	Classification.	λλ (Intensity).	νν.	Classification.
2758·76 (0)	36237·5	Q 9, 12	2653·68 (0)	37672·3	R^i 3, 4
58·49 (1)	241·0	R 9, 12	49·73 (4)	728·5	Q 1, 2*
56·31 (0)	269·7	R 9. 12	49·30 (2)	734·6	Q^i 1, 2*
49·83 (0)	355·2	Q 8, 11	47·50 (6)	760·3	Q 0, 1*
49·45 (1)	360·2	R 8, 11	47·08 (3)	766·2	Q 0, 1*
47·42 (0)	387·0	R^i 8, 11	45·25 (1)	792·4	Q 7, 7
42·28 (1)	455·3	Q 7, 10	44·92 (2)	797·1	R 7, 7
41·69 (1)	463·1	R 7, 10	44·22 (1)	807·1	R^i 7, 7
39·90 (0)	486·9	R^i 7, 10	38·55 (2)	888·3	Q 6, 6
35·92 (1)	540·0	Q 6, 9	38·10 (3)	894·8	Q^i, R 6, 6
35·01 (1)	552·0	R 6, 9	37·59 (1)	902·1	R^i 6, 6
34·35 (1)	561·0	Q^i 6, 9	32·80 (3)	971·1	Q 5, 5
33·43 (0)	573·3	R^i 6, 9	32·46 (0)	976·0	Q^i 5, 5
30·58 (1)	611·4	Q 5, 8	32·19 (3)	979·9	R 5, 5
29·07 (1)	631·6	Q^i R 5, 8	31·83 (1)	985·1	R^i 5, 5
27·57 (0)	651·8	R^i 5, 8	27·82 (4)	38043·0	Q 4, 4
26·06 (1)	672·1	Q 9, 11	27·55 (1)	046·9	Q 4, 4
25·83 (1)	675·2	R 9, 11	27·00 (3)	054·9	R 4, 4
17·10 (1)	793·1	Q 8, 10	26·74 (2)	058·7	R^i 4, 4
16·73 (1)	798·1	R 8, 10	23·54 (5)	105·1	Q 3, 3
15·11 (0)	819·9	R^i 8, 10	23·41 (2)	107·0	Q^i 3, 3
09·41 (2)	897·5	Q 7, 9	22·40 (4)	121·6	R 3, 3
08·95 (2)	903·7	R 7, 9	22·24 (2)	124·0	R^i 3, 3
07·97 (0)	917·1	Q^i 7, 9	19·98 (4)	156·9	Q 2, 2
07·56 (1)	922·7	R^i 7, 9	19·89 (2)	158·2	Q^i 2, 2
02·94 (2)	985·8	Q 6, 8	18·21 (3)	182·7	R 2 2
02·26 (3)	995·1	R 6, 8	16·97 (4)	200·5	Q 1, 1
01·70 (1)	37002·8	Q^i 6, 8	14·44 (8)	237·7	Q 0, 0, and R 1, 1
01·04 (1)	011·8	R^i 6, 8			
2697·43 (3)	061·3	Q 5, 7	10·22 (5)	299·5	R 0, 0
96·39 (3)	075·6	Q^i, R 5, 7	07·06 (1)	345·9	Q 6, 5
95·31 (1)	090·5	R^i 5, 7	06·68 (2)	351·5	R 6. 5
92·80 (5)	125·1	Q 4, 6	01·14 (3)	433·2	Q 5, 4
91·80 (2)	138·9	Q^i 4, 6	00·67 (3)	440·2	R 5, 4
91·12 (2)	148·2	R 4, 6	2596·04 (3)	508·7	Q 4, 3
90·13 (1)	161·9	R^i 4, 6	95·52 (1)	516·4	R^i 4, 3
85·68 (6)	223·5	Q 2, 4*	95·42 (2)	517·9	R 4, 3
85·05 (1)	232·2	Q 8, 9	91·64 (2)	574·1	Q 3, 2
84·82 (3)	235·4	Q^i 2, 4*	91·02 (1)	583·3	R^i 3, 2
84·56 (1)	239·0	R 8, 9	90·81 (2)	586·4	R 3, 2
83·11 (6)	259·1	Q 1, 3*	87·88 (1)	630·1	Q 2, 1
82·26 (3)	270·9	Q^i 1, 3*	86·98 (1)	643·6	R^i 2, 1
81·10 (4)	287·1	Q 0, 2*	86·72 (2)	647·4	R 2, 1
80·29 (2)	298·3	Q^i 0. 2*	84·70 (0)	677·6	Q^i1, 0
77·12 (0)	342·5	Q 7, 8	83·37 (0)	697·5	R^i 1, 0
76·71 (2)	348·2	R 7, 8	83·01 (0)	702·9	R 1, 0
76·13 (0)	356·3	Q^i 7, 8	75·74 (0)	812·2	R 6, 4
75·70 (1)	362·3	R^i 7, 8	70·40 (0)	892·8	Q^i 5, 3
70·47 (2)	435·5	Q 6, 7	70·02 (0)	898·6	Q, R^i 5, 3
69·93 (2)	443·0	R 6, 7	69·63 (1)	904·5	R 5, 3
69·10 (1)	454·7	R^i 6, 7	65·27 (0)	970·6	Q^i 4, 2
64·84 (2)	514·6	Q 5, 6	64·76 (1)	978·3	Q, R^i 4, 2
64·08 (2)	525·3	Q^i, R 5, 6	64·27 (1)	985·8	R 4, 2
63·35 (0)	535·5	R^i 5, 6	60·75 (0)	39039·4	Q^i 3, 1
60·06 (1)	581·9	Q 4, 5	60·16 (1)	048·4	Q, R^i 3, 1
59·46 (0)	590·4	Q^i 4, 5	59·60 (1)	056·9	R 3, 1
58·92 (2)	598·1	R 4, 5	56·87 (0)	098·6	Q^i 2, 0
58·31 (1)	606·7	R^i 4, 5	56·28 (0)	107·6	Q 2, 0
56·03 (1)	639·0	Q 3, 4	56·07 (0)	110·8	R^i 2, 0
55·45 (0)	647·2	Q^i 3, 4	55·46 (1)	120·2	R 2, 0
54·21 (1)	664·8	R 3, 4			

* Degraded away from red.

For completeness, particulars of a few faint bands which do not appear in the list of classified bands are given in Table VII. Some of these may possibly represent lines, as it was very difficult to distinguish faint band heads from faint lines unless places could be found for them in the vibrational analysis.

In addition to the bands, a few distinct lines also occur in the photographs of the aluminium chloride spectrum. The most prominent are due to aluminium (Al II) including λλ 2816·2 (4) 2660·39 (2), 2652·48 (5), 2631·60 (1),2 575·40 (2), 2575·12 (3) and 2568·00 (3). Other lines which appear with varying intensities, but are mostly faint, are due to silicon, from disintegration of the discharge tube, and to iron from a slight impurity in the aluminium electrodes. There are still other lines which are probably due to Cl II, namely, λλ 2687·95 (3),* 2620·19 (1), 2617·02 (4) and 2614·32 (3). Unidentified lines include strong lines at λλ 2688·90 (5),* 2614·19 (5) and fainter ones at λλ 2670·58 (1), 2636·44 (2).

Table VII.—Faint Unclassified Bands.

λλ Int.	νν.	λλ Int.	νν.
2810·12 (0)	35875·2	2759·47 (0)	36228·1
2788·19 (0)	855·0	2721·82 (1)	729·3
2779·88 (0)	962·2	2719·95 (1)	754·6
2777·90 (0)	987·8	2706·53 (0)	936·7
2777·48 (0)	993·3	2689·72 (0)	37167·6
2766·78 (0)	36132·5	2686·13 (1)	217·3

* [*Added in proof May* 1, 1934—Professor W. E. Curtis has pointed out to the authors that the two "lines" recorded at λλ 2688·90(5), 2687·95(3) (see Plate 8, *b*) closely agree in positions with the Q and Q^i heads which might be expected at $v'v'' = (3, 5)$. The wave numbers are respectively 37178·9 and 37192·0, while the position of the Q head calculated from the general formula is 37178·8 and the difference $\Delta\nu = 13\cdot1$ compares favourably, with the calculated isotope separation 12·4; the relative intensities are also appropriate to Q and Q^i. It is therefore very probable that Q (3, 5) marks a point at which the B values* for the upper (B′) and lower (B″) states are so nearly equal that the band lines of the Q and Q^i branches are superposed and thus present the appearance of simple lines or undegraded bands.

With this addition the $v'' - v' = 2$ sequence is complete from (0, 2) to (9, 11). From (4, 6) to (9, 11) the degradation is towards the red, and from (0, 2) to (2, 4) away from the red, (3, 5) being a transition stage. There must accordingly be a "crossing over" of the B values in this sequence near the (3, 5) bands; that is, for pairs of values of $v'v''$ greater

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* In the rotational term, $B = h/8\pi^2cI$, where I is the moment of inertia of the rotating molecule, and the other symbols have their usual meanings.

Summary.

A band system having its greatest intensity at λ 2610 has been photographed with high dispersion in vacuum tubes containing the vapour of aluminium chloride. The system extends from λ 2555 to about λ 2810, and with a few important exceptions, the bands are degraded to the red. The heads of the bands occur in pairs which have been interpreted as representing R and Q branches. Along with the main bands due to the lighter molecules $AlCl^{35}$ there are associated bands which originate in the heavier molecules $AlCl^{37}$ and are displaced in accordance with theoretical expectation.

An unusual feature of the band system is the occurrence of two short sequences of bands which are degraded away from the red, in opposition to the remaining bands. These have low vibrational quantum numbers and are

than (3·5), (B′ − B″) must be negative, while for smaller values it must be positive. The observations also show that there is a similar crossing over in the $v'' - v' = 1$ sequence.

In the absence of rotational analyses, the B values are not known, but Professor Curtis has suggested a procedure by which relative values of (B′ − B″) derived from separations of the R and Q heads in the "normal" bands may be extrapolated to give approximate values for the bands which are degraded in the opposite direction. In this way it can be shown that a change of sign of (B′ − B″) is to be expected in the positions where the bands degraded away from the red are observed.

Theory (Jevons' Report, p. 44) gives

$$\nu_R - \nu_Q = -\frac{(B' + B'')^2}{4(B' - B'')}$$

and since (B′ + B″) will vary relatively slowly with v, the (B′ − B″) values will be approximately proportional to the reciprocals of $\nu_R - \nu_Q$. Reciprocals of the separations of the normal R and Q heads given in Table IV were accordingly arranged in a $v'v''$ table, and were found to show a definitely linear decrease of the negative values of (B′ − B″) with increasing v'', while they increased with v' more rapidly than a linear law would indicate. Extrapolation then gave positive values for (0·1), (0·2), (1·3), (2·4) and sensibly zero for (1·2). Small negative values were found for (2·3) and (3·5). The band (2, 3) is not recorded in the observations, but interpolation of its position suggests that the Q head is probably obscured by the strong aluminium line λ 2652·48 (ν 37689·4), and re-examination of the photographs has shown that there is a faint line or band which may represent the Q head; comparison with other members of this sequence suggests that (2, 3) would not be a strong band.

Notwithstanding the low degree of accuracy of the (B′ − B″) values obtained in this way, these results provide a satisfactory interpretation of the reversed direction of degradation of some of the bands which appear in AlCl, and of the occurrence of undegraded bands. In the bands degraded away from the red, P heads should occur instead of R, but these have not been noted. They would be expected to appear at relatively large distances from the Q heads, and they may thus be observed by adjacent bands, or be too feeble for observation.]

of correspondingly high intensity. The close agreement with the positions calculated for them, together with the displacements of the accompanying isotope heads, shows that these bands are part of the same system as the bands which are degraded to the red.

The vibrational analysis and the discussion of the isotope bands combine to prove that the band system under investigation originates in the diatomic molecules $AlCl^{35}$ and $AlCl^{37}$.

Investigations in the Infra-red Region of the Spectrum. Part X.—*The Asymmetrical Molecule Nitrosyl Chloride*, NOCl.

By C. R. Bailey and A. B. D. Cassie, the Sir William Ramsay Laboratories of Inorganic and Physical Chemistry, University College, London.

(Communicated by F. G. Donnan, F.R.S.—Received January 20, 1934.)

The infra-red absorption spectrum of nitrosyl chloride was investigated with two objects in view. Firstly, if the substance is a covalent compound with normal valency linkings, the molecule will probably be asymmetrical and triangular. If this is so, the absorption bands will show no pronounced branch maxima such as are predicted and observed for symmetrical molecules, and the presence or absence of these maxima in the same conditions of resolution and concentration provides a test of the theory according to which the spectra of such gases as SO_2, ClO_2, and Cl_2O have been interpreted. The two former molecules are required by the theory to be symmetrical, although such symmetry is not to be expected from the ordinary rules of valence. The experimental fact that the characteristic P, Q, and R branch maxima are absent in NOCl thus provides a verification of the theory.

Secondly, six electrons are effectively available for binding in the molecule, and accordingly* the structure should be triangular with a vertical angle ONCl approximately 120°, and governed by a valence force system. The molecule should, therefore, show whether or not the structure of triatomics is determined primarily by the number of available binding electrons.

Experimental.

The absorption spectrum of NOCl prepared by heating dry sodium chloride with nitrosylsulphonic acid shows that such specimens are contaminated with explosion; but, on the other hand, cordite, although it contains as much as 58 per cent. nitro-glycerine, owing to the fact that it contains also vaseline, gives a temperature lower than that of ballistite containing only 30 per cent. nitro-glycerine and no vaseline. Of course, the minimum deflection is the one due to gun-cotton, which contains no nitro-glycerine.

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* Cassie, 'Nature,' vol. 131, p. 438 (1933).

Similar experiments have also been repeated with other explosives and with different charges, and, in every case, the same comparative results have been obtained.

The above refers only to a part of the experiments which have been carried out so far. Another series is now in progress for determining the other necessary elements which will be required before we can accurately express the value of these deflections of the galvanometer in degrees of temperature. One important element which comes into play is the inertia of the galvanometer itself in connection with the shortness of the time during which the maximum temperature exists, and there are also other points which are being investigated, and these will form the subject of a further communication.

We have, however, thought it advisable not to delay communicating the above results, as already the described method shows the possibility first of all of obtaining approximately an idea of the temperature during explosion, and, secondly, it shows a clear way by which the comparative temperatures for various explosives can be determined. These, taken in connection with the results shown in our former communication, will serve, we hope, to give a better knowledge of the different modern explosives which are now commonly used.

"The Spectrum of α Aquilæ." By SIR NORMAN LOCKYER, K.C.B., F.R.S., and A. FOWLER. Received January 18,—Read February 8, 1900.

[PLATE 1.]

The study of enhanced lines throws considerable light on the spectrum of α Aquilæ, the peculiarities of which were first described by Professor Pickering* and Dr. Scheiner† in 1889. In this spectrum the lines of hydrogen are strong and broad, but the additional lines, instead of being faint and sharp as in most other stars of this class, are faint and diffuse. Dr. Scheiner stated that these apparent bands were identical with the most conspicuous groups of lines in the solar spectrum, and further that this appearance of the spectrum can be imitated by holding a rather faint drawing of the solar spectrum at such a distance that the individual lines are no longer visible.

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* Third Annual Rep. Henry Draper Memorial, p. 5.

† 'Ast. Nach.,' 2924.

From a consideration of the photographs taken at Harvard College Observatory, Professor Pickering suggested in 1891 that the diffuseness of the lines in the spectrum of α Aquilæ and certain other stars was perhaps due to a rapid rotation of the star.* That rotation might be capable of producing such effects had already been suggested by Abney in 1877.†

Photographs taken at Kensington with large dispersion, during 1892, led to the adoption of Professor Pickering's view, and the spectrum of α Aquilæ was classed with that of β Arietis, in which we apparently got the same lines quite sharp.‡

In 1895 Dr. Scheiner again referred to this spectrum,§ and suggested that it represents a transition stage from the first to the second type; as an alternative explanation, he mentions the view that the spectrum may be a composite one, in which a spectrum of the first type is superposed upon one of the second.

In a recent paper|| Dr. Vogel has discussed the spectrum of α Aquilæ chiefly with reference to its motion in the line of sight, but he also considers the question of the haziness of the lines. He refers to some experimental photographs which depict the solar spectrum with its lines broadened by a cylindrical lens, or by a photograph taken out of focus, and states that spectra of this kind have been obtained in which the close lines run together so as to produce a spectrum resembling that of α Aquilæ. He adds that the exact comparison of the two spectra shows that the agreement is not perfect, in particular that the G group is hardly indicated in the spectrum of α Aquilæ, while it comes out strongly in the solar spectrum when thrown out of focus. He accordingly places the spectrum of α Aquilæ in his Class I*a* 3, of which α Cygni, β Cassiopeiæ, and Procyon are members,¶ and further concludes that the lines are broadened in consequence of rapid rotation, without, however, referring to previous suggestions to the same effect.

The general result is that while Vogel classes α Aquilæ with α Cygni, which, on the meteoritic hypothesis, is a star of increasing temperature, the work at Kensington indicates that it should be classed with stars like β Arietis, which there is every reason to believe to be cooling. This difference as to facts is so important that the whole question has been re-investigated.

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* 'Annals Harv. Coll. Obs.,' vol. 26 (1891), Pt. I, p. 21.

† 'Monthly Notices R.A.S.,' vol. 37, p. 278.

‡ 'Phil. Trans.,' A, vol. 184 (1893), p. 697.

§ 'Pub. Ast. Obs. zu Potsdam,' vol. 7, Part II, p. 232.

|| 'Sitzber. Akad. Berlin,' Nov. 1898; translated in 'Astrophys. Journ.,' Jan. 1899.

¶ 'Astrophys. Journ.,' vol. 2 (1895), p. 346.

The Kensington Photographs.

An investigation of the spectrum of α Aquilæ was commenced at Kensington in 1890, and, with the various instruments employed up to 1892, fifteen negatives were obtained.* In all these the lines were ill defined, and it was decided to take a special series of photographs "in order to determine whether the haziness of its spectrum lines is invariable."† Since then a considerable number of photographs has been obtained, but although variations have been suspected it is found difficult to establish their reality. One thing seems quite certain, namely, that the lines are always ill defined.

At the Royal Society Conversazione in 1894, enlarged copies of photographs of the spectra of α Aquilæ and β Arietis were exhibited which indicated that Pickering's view that the haziness of the lines is due to rotation is probably correct.

Dr. Scheiner's experiment of photographing the solar spectrum out of focus has since been repeated; but while it was found possible to produce bands in this way, only a few of them agree with those in α Aquilæ. Among these coincident bands are 4031—4036 (Mn), 4046 (Fe), 4064 (Fe), 4132—4135 (chiefly Fe), 4143·6—4144 (Fe), 4226·9 (Ca), 4250·3—4251 (Fe), 4260·2—4260·6 (Fe), 4271·3—4271·9 (Fe).

On the other hand, by taking an out-of-focus enlargement of a negative of the spectrum of β Arietis, the violet being put more out of focus than the blue, the spectrum of α Aquilæ is almost perfectly reproduced (see Plate). The difference in width of the bands appears to be sufficiently explained by the gradually increasing dispersion in prismatic spectra as the violet end is approached. With the instrument employed at Kensington a tenth-metre near λ 4046 is represented by a distance on the photographs about 1·4 times as great as that corresponding to the same difference of wave-length near λ 4384; and since the velocity which would produce a displacement of one-tenth metre at λ 4384 would produce a displacement of 0·92 tenth-metre at λ 4046, the displacements on the photographs for the same velocity, with the particular instrument employed, will be in the proportion of 1 to 1·29 at λ 4384 and λ 4046 respectively.

Classification of the Star.

This experiment appears to be a sufficient demonstration of the essential similarity of the spectra of α Aquilæ and β Arietis, so that the former conclusion that the two stars should be classed together is perfectly justified.

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* 'Phil. Trans.,' A, vol. 184 (1893), pp. 685–688.

† *Ibid.*, p. 696.

According to the earlier work at Kensington, stars like β Arietis were classed in Group $V\alpha$,* that is, between stars like Sirius and those like Procyon. The work on enhanced lines which has been done since then enables us to carry on the work of classification with much greater precision, since we have now a means of estimating relative temperatures with considerable accuracy. In this way we learn that stars at each stage of temperature fall into two groups, one of which represents stars of increasing temperature, and the other including stars of decreasing temperature. α Aquilæ and β Arietis fall in the latter group, and are to be regarded therefore as stars in which photospheres have formed. The later work on the classification of spectra has shown that it is sufficient for all practical purposes to include both in the Sirian group of stars.

This question of classification is further elucidated by a more detailed examination of the spectrun of α Aquilæ in relation to α Cygni and the Sirian stars. The foregoing demonstration of the likeness between α Aquilæ and β Arietis leads us to expect that the origins of the lines in the spectrum of α Aquilæ will be the same in the main as those of β Arietis and Sirius. In these stars the temperature of the absorbing vapours is intermediate between that of the arc and that at which enhanced lines appear alone, so that the spectra show both arc and enhanced lines. The origins of the chief enhanced lines in the spectrum of Sirius have already been investigated,† and practically the same lines occur in β Arietis. Besides these enhanced lines there are several well-known arc lines, such as the iron triplets and the blue line of calcium, which can be readily identified. The origins of some of the lines of both classes are shown in the plate which accompanies this paper, enhanced lines being shown at the bottom and arc lines at the top.

It will be seen that enhanced lines of iron appear in α Aquilæ, but have not the same relative intensity as in α Cygni; the most enhanced line of iron (λ 4233·3), for example, which in α Cygni is represented by a very strong and well-defined line, is in α Aquilæ very weak and hazy. On the other hand, some of the enhanced lines of iron less refrangible than $H\gamma$ are fairly prominent. The principal enhanced lines of magnesium, strontium, and titanium are also certainly present, as shown in the plate. The enhanced double line of silicium at λλ 4128·1, 4131·1, if present, is very weak, a moderately strong hazy line, rather less refrangible than the silicium double, making it rather difficult to determine whether the latter is certainly present.

Among the arc lines present are those of the iron triplet in the violet (λλ 4045·90, 4063·76, 4071·79), which are clearly seen, but the iron triplet in the blue (λλ 4383·70—4415·27) cannot be identified with certainty. The place occupied by the manganese quartet ($\lambda\lambda$ 4030·88—4035·88) is covered in the spectrum of the star by what appears to be a broad hazy line, which is probably composed of the individual components of the quartet merged together. The arc line of calcium at λ 4226·90 is one of the most prominent lines in the spectrum.

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* 'Phil. Trans.,' A, vol. 184 (1893), p. 726.

† 'Roy. Soc. Proc.,' vol. 65 (1899). Plate 7.

The classification of the spectrum of α Aquilæ may therefore be considered as settled; it does not sufficiently resemble α Cygni to justify Vogel's view that it should be classed with that type of star, while, on the other hand, apart from the haziness of the lines, it does bear a very strong resemblance to β Arietis and other Sirian stars, and should therefore be classed with them.

[*Note, February* 8.—In a later publication* Vogel places α Cygni in his Class I*a* 2, with Sirius, β Arietis, &c., but this does not materially modify the conclusions arrived at.]

There are other points on which this demonstration of the similarity of α Aquilæ and β Arietis may be brought to bear, among them being the determination of the lines most suitable for the measurement of the velocity of the star in the line of sight, and the approximate determination of the velocity of rotation necessary to produce the observed haziness of the lines.

Lines suitable for the Determination of the Velocity of the Star in the Line of Sight.

For the measurement of the velocity of α Aquilæ, Deslandres has employed comparison spectra of hydrogen, iron, and calcium.† Vogel, however, questions the advantage of using the spectra of iron and calcium as comparisons for this purpose, on the ground that "the lines in the spectrum of α Aquilæ are so diffuse . . . . that between H_β and H_δ no lines except those of hydrogen and the magnesium line at λ 4481 can be identified with known lines." He himself has used the H_γ line alone as a term of comparison, and concludes that there are no indications of a periodic change in the velocity of the star in the line of sight, such as was supposed by Deslandres.

We now know with certainty the origins of a considerable number of the lines in α Aquilæ, so that measurements of the velocity of the star are placed on a surer basis. Since the spectrum of α Aquilæ is simpler than that of the sun, some of the broad lines do not represent confused groups of lines, but are broadened individual lines. The latter class of lines, when of known origin, seems to be well adapted for the

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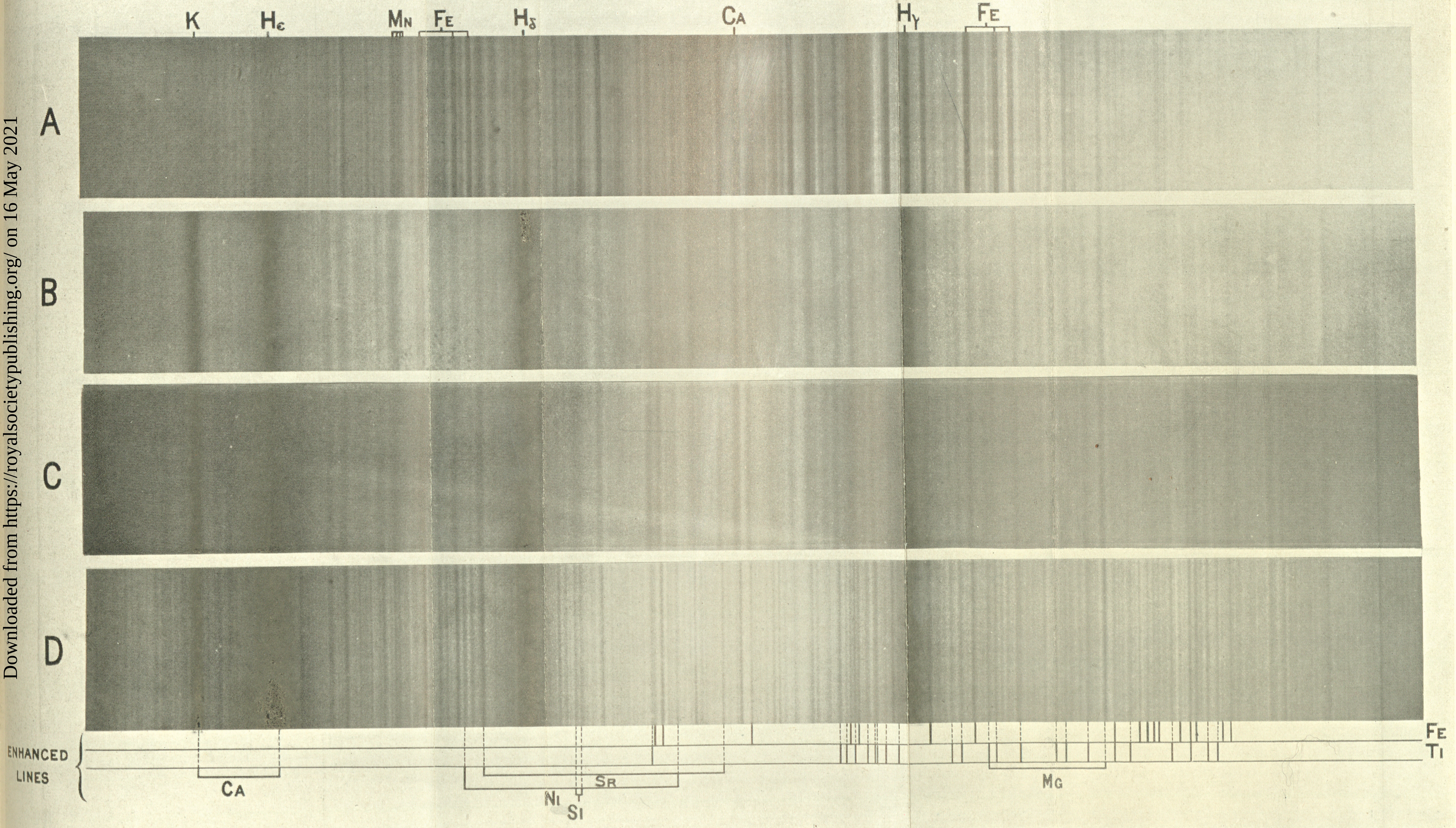
* 'Pub. Ast. Obs. Potsdam,' 1899, vol. 12, Part I, p. 49.

† 'Comptes Rendus,' vol. 121 (1895), p. 629.


K
Hε
Mn
Fe
Hδ
Ca
Hγ
Fe
A
B
C
D
ENHANCED LINES
Ca
Ni
Si
Sr
Mg
Fe
Ti

measurement of the velocity of the star, for though they may be still somewhat wide, they are much less so than the lines of hydrogen. Among these broadened individual lines are:—

Iron (enhanced lines).—4178·95, 4233·25, 4385·55, 4549·64.
„ (arc lines).—4045·90.
Titanium (enhanced lines).—4417·98, 4443·98.
Strontium.—4215·66.

The enhanced line of magnesium at 4481·3 is usually sharply defined in stellar spectra, but the fact that it is generally fluffy in the comparison spark disqualifies it for accurate measurements.

The Velocity of Rotation.

Assuming that β Arietis represents the spectrum of α Aquilæ as it would appear if the axis were directed towards the earth, we can get a general idea of the velocity of rotation necessary to produce the observed broadening of the lines. For this purpose lines which occur in groups are obviously unsuitable, but we can utilise the lines to which attention has just been drawn. Taking the enhanced line of iron at λ 4178·95, we find that its thickness is increased from about two to four tenth-metres, and this corresponds to a surface velocity of the star at the equator of about 45 miles per second, supposing that the axis is perpendicular to the line of sight. Similar measurements of the broadening of the magnesium line 4481·3 yield a velocity of about 40 miles per second. Since only a small portion of the surface of the star would exhibit the effects of the maximum velocity, it is probable that these values are too low, really representing the equatorial velocity of rotation resolved along the line of sight with reference to a point somewhere between the limb and centre of the star.

Dr. Vogel gives reasons in his paper for supposing the velocity of rotation to be possibly 27 kilometres (16·8 miles) per second, but this determination does not depend upon measurements of individual lines.

General Conclusions.

The investigation of the Kensington photographs of the spectrum of α Aquilæ has thus led to the following conclusions:—

(1) Apart from the general haziness of the lines, the spectrum presents no unfamiliar features.

(2) The spectrum is of the Sirian type, showing enhanced lines of various metals, and a smaller number of arc lines.

(3) A rapid rotation of the star, as first suggested by Pickering, appears to be a simple and sufficient explanation of the peculiarities of the spectrum.

DESCRIPTION OF PLATE.

A. Solar spectrum, purposely out of focus.
B. α Aquilæ.
C. β Arietis, purposely out of focus.
D. β Arietis, in focus.

The photographs of the spectrum of α Aquilæ which have been obtained at Kensington since 1890 were nearly all taken by Messrs. Fowler, Baxandall, Shackleton, and North. Mr. Baxandall has assisted in the determination of origins.

The photographic plate has been prepared from the original negatives by Sapper Wilkie, R.E.

"The Velocity of the Ions produced in Gases by Röntgen Rays."

By JOHN ZELENY, B.Sc., B.A., Assistant Professor of Physics, University of Minnesota. Communicated by Professor J. J. THOMSON, F.R.S. Received February 15,—Read March 1, 1900.

(Abstract.)

The sum of the velocities with which the positive and the negative ions that are produced in gases by the Röntgen rays move when in a unit electric field has already been determined by an indirect method by E. Rutherford.[*] In the experiments here described the velocity was determined in a number of gases for the positive and negative ions separately, by comparing the ionic velocity directly with that of a stream of gas. The stream of gas was made to flow between two concentric cylinders, which were maintained at different potentials. By passing a narrow beam of Röntgen rays through the cylinders at right angles to their length, a narrow layer of ionised gas was produced. Due to the electric field between the two cylinders, the ions of this layer tended to move radially towards, or away from, the axis of the cylinders, but at the same time they were carried along by the stream of gas. Of the ions of this layer which travelled inwards, those that started from the inner surface of the outer cylinder were carried a distance X by the gas stream before they reached the surface of the inner cylinder.

This distance is dependent directly upon the mean velocity of the gas stream, and inversely upon the difference of potential between the two cylinders. For obtaining the difference of potential which must be used to allow the ions to be carried a certain distance along the tubes by the gas stream the inner cylinder was divided at some distance from the beam of rays into two parts, insulated from each

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[*] E. Rutherford, 'Phil. Mag.,' November, 1897.

"On a New Series of Lines in the Spectrum of Magnesium." By A. FOWLER, A.R.C.Sc., F.R.A.S., Assistant Professor of Physics, Royal College of Science, South Kensington. Communicated by H. L. CALLENDAR, F.R.S. Received March 9,—Read March 26, 1903.

Although the spectrum of magnesium has been the subject of many investigations, certain lines which occur in the arc spectrum appear to have hitherto escaped notice. The lines in question are comparatively feeble, but on account of their theoretical interest it seems desirable to draw attention to them.

The new lines make their appearance in the spectrum when the arc is made to pass between poles consisting of magnesium rods, but they do not always appear with equal intensity. They are somewhat nebulous, especially on their less refrangible sides, so that their positions cannot be determined with great accuracy; but as nearly as they can be ascertained with the instruments at my disposal, the wave-lengths are (in air), 4511·4, 4251·0, 4106·8, and 4018·3.

A mere inspection of the photographs suggests that these lines constitute a regular series, associated with the much stronger series described by Rydberg*, having wave-lengths 5528·75, 4703·33, 4352·18, 4167·81, 4058·45, and 3987·08, according to the measures of Kayser and Runge. This view seems to be sufficiently confirmed by calculation.

Rydberg found that neither his own general formula nor that of Kayser and Runge could be applied with sufficient accuracy to the stronger series, and employed a combination of the two formulæ, namely,

$$n = a + \frac{b}{(m+\mu)^2} + \frac{c}{(m+\mu)^4},$$

where n is the oscillation frequency, m has the values 3, 4, 5, &c., and a, b, c, and μ are constants to be determined from four lines belonging to the series. For the magnesium series, the equation calculated by Rydberg is

$$n = 26{,}631{\cdot}44 - \frac{111{,}856{\cdot}92}{(m+0{\cdot}406)^2} + \frac{147{,}764{\cdot}05}{(m+0{\cdot}406)^4},$$

n being the oscillation frequency *in air*, and m having the values 3, 4, 5, 6, 7, 8 for the six lines named above.

Using the same formula for the new series, and calculating the constants from the four lines, the equation for frequencies *in vacuo* is

$$n = 26{,}595{\cdot}4 - \frac{102{,}496{\cdot}6}{(m+0{\cdot}618)^2} + \frac{168{,}840{\cdot}5}{(m+0{\cdot}618)^4}.$$

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* 'Öfversigt af Kongl. Vet. Akad. Forhandl.,' 1893, Stockholm.

Another formula* which may be conveniently employed is

$$n = n_\infty - \frac{C}{(m+\mu)^2 - m_0}.$$

This formula gives for the two magnesium series the equations:

$$\text{“ Rydberg ” series,} \quad n = 26{,}601{\cdot}49 - \frac{107{,}071{\cdot}37}{(m + 1{\cdot}2304)^2 + 2{\cdot}13282},$$

$$\text{New series,} \quad n = 26{,}587{\cdot}4 - \frac{100{,}033{\cdot}6}{(m + 0{\cdot}495)^2 + 2{\cdot}38919},$$

n being the oscillation frequency *in vacuo* in each case.

It will be seen that the convergence frequency of the new series is as nearly equal to that of the Rydberg series as can be expected with the comparatively rough wave-lengths employed, and it may be added that in each case the constant m_0 is of unusual magnitude. These facts, in conjunction with the general characters and relative intensities of the lines, render it highly probable that the new series is associated with the Rydberg series as second and first subordinate series respectively.

Applying the formula to the calculation of the members of the new series for which $m = 3$ and $m = 2$, the corresponding wave-lengths in air are 5065·0 and 6674·5. The first is probably represented by a line having an approximate wave-length 5067, which is not so readily observed in the photographs as the others, because the plates employed are comparatively slow for this part of the spectrum, and if the exposure be lengthened, the banded spectrum of magnesium becomes strong enough to almost mask the line. The line 6674·5 is perhaps too far in the red to be conveniently observed, seeing that it is probably feeble and not well defined.

It may be reasonably concluded that the arc spectrum of magnesium includes two subordinate series of single lines in addition to the two well-known subordinate series of triplets. No such combination of series appears to have been previously noted in the spectrum of a metal, but two sets of series, each set consisting of a principal and two subordinate series, are well-known in the spectra of helium and oxygen.

The author desires to express his obligations to Mr. Herbert Shaw for valuable assistance in making the computations involved in investigating the various formulæ which have been suggested for series, as applied to the series which forms the subject of the present paper.

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* After much labour, this formula was arrived at by Mr. Herbert Shaw and the author as the one giving the most consistent results for series in general, but it was afterwards found that a similar formula, expressed in wave-lengths, had already been employed by Mr. Rummel (‘Roy. Soc. Victoria Proc.,’ vol. 10, Part I, 1897, p. 75).

"The Spectra of Metallic Arcs in an Exhausted Globe." By A. Fowler, A.R.C.Sc., F.R.A.S., and Howard Payn, F.R.A.S. Communicated by Sir Norman Lockyer, K.C.B., LL.D., F.R.S. Received June 10,—Read June 18, 1903.

[Plate 14.]

Working on the supposition that the bands which occur in the arc spectrum of magnesium are due to possible combinations of the metal with gases in the outer part of the arc, we have recently attempted to obtain the line spectrum free from bands by photographing the spectrum when the arc is passed in an exhausted globe. It is found, however, that while the band beginning at λ 5007·5 is sometimes greatly reduced in intensity under these conditions, the bands attributed to "magnesium hydride" by Messrs. Liveing and Dewar* are very strongly developed.

Besides this, the characteristic spark, or "enhanced" line at λ 4481·3, which is almost invisible in the ordinary arc in air, is one of the strongest lines in the spectrum. Special interest attaches to this line on account of its application to the determination of relative stellar temperatures, based on the variations in the spectrum of magnesium under different conditions, which were first systematically investigated in relation to temperature by Sir Norman Lockyer in 1879.†

The occurrence of the line 4481 in the arc spectrum under special conditions was first recorded by Liveing and Dewar in 1888‡, and has since been investigated by other observers. Crew§ found that the line appeared in the spectrum of magnesium when the arc was surrounded by an atmosphere of hydrogen, and a little later Porter|| found among other results, that a similar effect was produced by oxygen. Experiments by Sir Norman Lockyer and the writers have confirmed these observations.

More recently, Hartmann and Eberhard¶ have observed that enhanced lines appear in the arc spectra of magnesium, zinc, and cadmium when the arc is made to pass in water. The spectra obtained in this manner are stated to be almost identical with those obtained when the arc is passed in a current of hydrogren, and the opinion is expressed that the change is produced by hydrogen released by electrolysis around the electrodes in water. Hartmann has since found

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* 'Roy. Soc. Proc.,' vol. 32, p. 196.

† 'Roy. Soc. Proc.,' vol. 30. p. 29; also 'Chemistry of the Sun,' p. 242; and 'Inorganic Evolution,' p. 75.

‡ 'Roy. Soc. Proc.,' vol. 44, p. 241.

§ 'Astrophys. Journ.,' vol. 12, p. 167, 1900.

|| 'Astrophys. Journ.,' vol. 15, p. 281, 1902.

¶ 'Sitz. der Preuss. Akad. der Wiss.,' 1903, IV, p. 40; 'Astrophys. Journ.,' vol. 17, p. 229.

that the magnesium line 4481 becomes stronger in the spectrum of the metallic arc in air as the current strength is lessened.*

The occurrence of enhanced lines in the spectrum of the arc at reduced pressure, however, does not appear to have been previously recorded, and it may, therefore, be useful to state briefly the results which have been obtained.

Method of Experiment.

The experiments were conveniently made by enclosing the arc in a glass globe of about a litre capacity having two necks and an outlet by which connection was made with a Töppler pump. Short rods of the metal to be experimented upon were attached to brass rods passed through the two necks and made air-tight with a packing of rubber tube and Chatterton's compound.

The pole pieces were put nearly in contact, so that a slight pressure on one of them sufficed to strike the arc. With this arrangement the arc can only be observed for a comparatively short time owing to the burning away of the poles, and the experiment is also interrupted by the formation of a deposit on the interior of the globe. Still it is usually possible to take two or three photographs in each setting up of the apparatus. Ordinary commercial metals cast into rods a quarter of an inch in diameter were used.

[*Note added July* 16.—In each case the exhaustion was carried as far as the nature of the apparatus would permit. The pressure on starting the arc was from 1 to 2 mm.

The current was obtained from a 100-volt circuit, and in a repetition of the experiment with magnesium poles, measurements have shown that the current strength usually employed was 7 ampères for the arc in air and 8 for the arc under reduced pressure.]

Magnesium.

The well-known triplets beginning at 5183·84 (b_1) and 3838·44 are apparently little affected when the globe is exhausted, but the lines 5528·75, 4703·33, 4352·18, 4167·81, 4058·45, and 3987·08, which form a regular series,† are usually sharper than in the ordinary arc, and in some photographs four additional members of the series are seen (approximate wave-lengths 3938, 3904, 3879, 3860).

The band 5007·5, as already remarked, is generally reduced in intensity, while the "hydride" bands, beginning at 5618, 5210, 4849, appear with great intensity. Flutings of nitrogen also appear in some of the photographs.

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* 'Sitz. der Preuss. Akad. der Wiss.,' 1903, XII, p. 234; 'Astrophysical Journ.,' vol. 17, p. 270.

† Rydberg, 'Öfversigt af Kongl. Vet. Akad. Forhandl.,' 1893, Stockholm.

The enhanced line 4481·3 is of about the same intensity as b_1, and stronger than the lines 4703 and 4352. It is also notably sharp as compared with its usually hazy appearance in the spark spectrum of the metal.

Two conspicuous pairs of sharply defined lines which appear at approximate wave-lengths 4385, 4391 and 4428, 4434 cannot be traced to any known impurities, and a comparison with the spark spectrum leaves no doubt that they are true enhanced lines of magnesium. They are very ill-defined in the ordinary spark, but are distinctly visible as double lines in a photograph of the spark spectrum when a small amount of self-induction is introduced into the secondary circuit, though disappearing when the self-induction is increased. The line at 4391 is apparently identical with the enhanced line recorded by Sir Norman Lockyer* at 4395. Porter† has observed lines at approximate wave-lengths 4390, 4430 and 4434 in the spectrum of the magnesium arc in an atmosphere of ammonia or oxygen which probably correspond with three of the above four lines, but states that he has not succeeded in identifying them.

Another spark line of small intensity recorded by Thalèn and others at λ 4587 does not appear in the photographs of the spectrum of the arc in the exhausted globe, but Porter finds it among the lines of the magnesium arc in ammonia.

It is important to note also that in some of the photographs there is a distinct line coincident with the F (H_β) line of hydrogen.

[*Note added July* 16.—The identification of this line has been confirmed by visual observations showing the presence of both H_β and H_α.]

Another point of importance, in considerations as to temperature conditions, is that the flutings and enhanced lines appear to originate in different parts of the arc.

Zinc.

The strong triplet of lines at λλ 4810·71, 4722·26, 4680·38, and the adjacent line 4630·06, appear as strong lines, but are generally sharper than the corresponding lines in the spectrum of the arc in air at atmospheric pressure. Most of the other lines in the region D to K disappear altogether or are greatly reduced in intensity.

The well-known spark lines 4912·2, 4924·8 (Thalèn's wave-lengths corrected to Rowland's scale) make their appearance with considerable intensity, though they are less striking than the principal enhanced lines which appear in the case of magnesium (Plate 14).

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* 'Roy. Soc. Proc.,' vol. 61, p. 163.

† 'Astrophys. Journ.,' vol. 15, p. 277.

Strong flutings also appear, the principal one commencing with a sharp head near λ 4300 and grading off towards the violet. These are identical with flutings which appear in the spectrum of the arc when zinc poles are surrounded by an atmosphere of hydrogen, and may therefore be provisionally attributed to "zinc hydride." These flutings have also been observed in the zinc arc in hydrogen by Basquin,* who also "in lieu of a better hypothesis" attributes them to a compound of hydrogen with the metal.

In one experiment the stronger flutings of nitrogen appeared in the spectrum, but they were apparently restricted to the region surrounding one of the poles. The F line of hydrogen also appears in some of the photographs.

As in the case of magnesium, there is evidence that the flutings and enhanced lines do not originate in the same part of the arc.

Cadmium.

The phenomena are generally similar to those observed in the case of zinc, but some of the features are less marked. The strong triplet λλ 5086·06, 4800·09, 4678·37 and the adjacent line 4662·69 are of reduced intensity, but more sharply defined than in the ordinary arc, while most of the other arc lines in the region D to K disappear. The spark lines 5379·3, 5338·6 are certainly present but not conspicuous.

Strong flutings, fading towards the violet, are seen, the principal heads having approximate wave-lengths, 4491 and 4298. Here, again, the flutings are identical with those which appear when the cadmium arc is surrounded by hydrogen, and may therefore be provisionally regarded as originating in "cadmium hydride."

The F line of hydrogen, if present, is too feeble to be shown in the photographs.

Iron.

It is only after careful examination that the spectrum of an iron arc in an exhausted globe is seen to be materially different from that of the arc in air at atmospheric pressure. Nevertheless, there is no doubt as to the appearance of the principal enhanced lines, among them being 5018·13 and 4584·02.

The F line of hydrogen is not certainly present, but it could not be distinguished from the neighbouring iron line with the dispersion employed unless comparatively strong.

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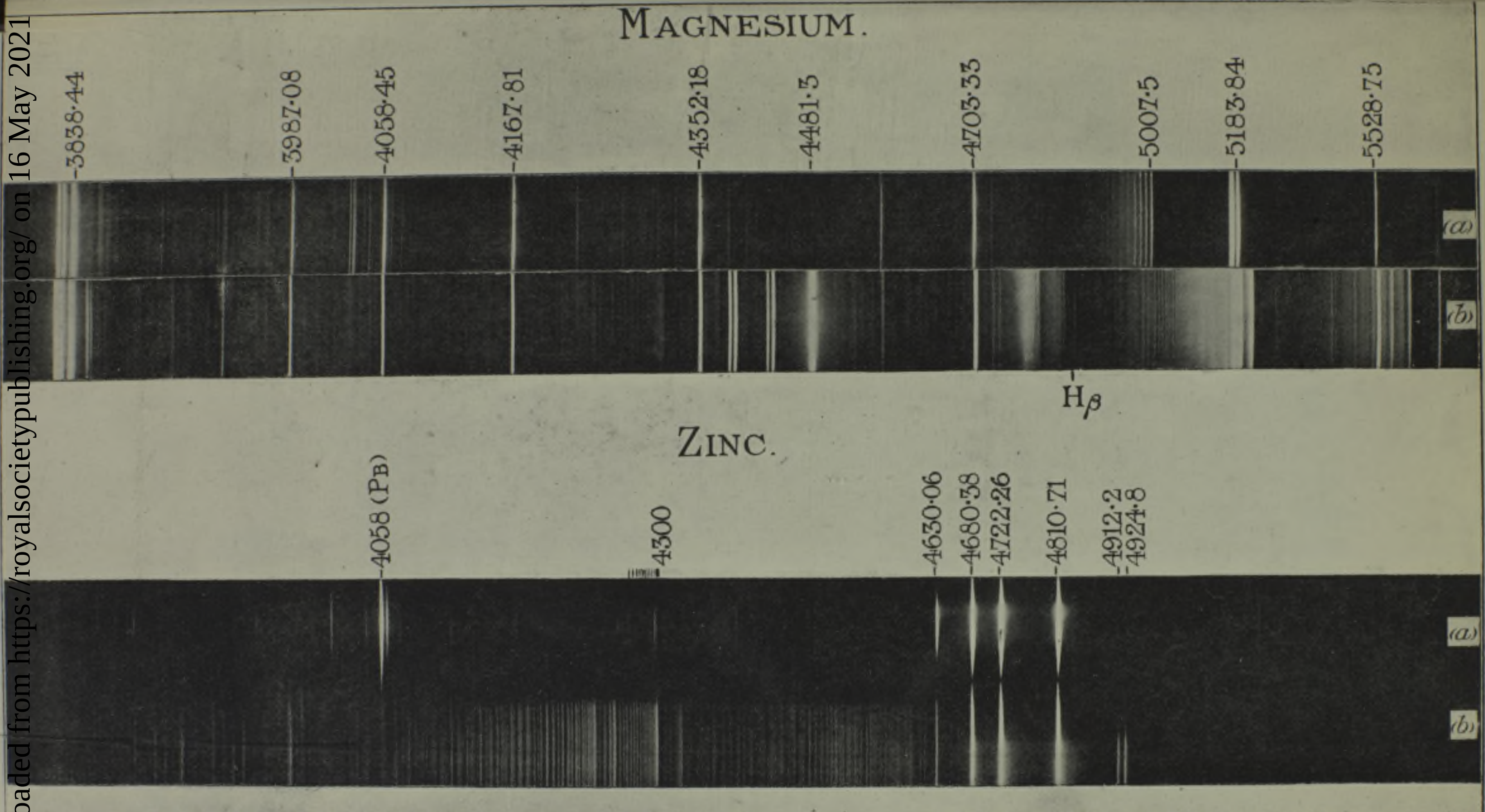
* 'Astrophys. Journ.,' vol. 14, p. 10, 1901.

Fowler and Payn.



(a) ARC IN AIR AT ATMOSPHERIC PRESSURE (b) ARC IN EXHAUSTED GLOBE.

Roy. Soc. Proc., vol. 72, Plate 14.

General Conclusion.

So far as they go, the experiments seem to suggest that the modifications of the arc spectra in an exhausted globe may be due to the presence of hydrogen liberated from the heated poles. It has already been pointed out that one of the effects of a hydrogen atmosphere on a metallic arc is to introduce enhanced lines into the spectrum, and the presence of hydrogen under the new conditions of experiment is indicated in the case of magnesium and zinc by the appearance of the H_β line, and in magnesium, zinc, and cadmium by flutings which are known to appear in the presence of hydrogen.

It is well known that hydrogen is occluded by many metals, and experiments made to determine the relative amounts of the gas given off on heating *in vacuo* show that the amounts are roughly proportional to the relative strengths of the enhanced lines appearing when the arc passes in the exhausted globe; that is, magnesium and zinc gave off the greatest quantities of the gas, cadmium the least, and iron an intermediate amount. The apparent absence of the F line in the spectra of cadmium and iron in the exhausted globe may, therefore, be due to its feeble intensity on account of the smaller quantity of gas driven out, while the absence of "hydride" bands in the case of iron may perhaps be explained by supposing that combination of hydrogen with iron does not readily take place.

The exact nature of the action of hydrogen on the arc requires further investigation.

The experiments described in the foregoing paper have been made in Sir Norman Lockyer's laboratory, to whom we desire to express our thanks for the privileges afforded. We also wish to express our thanks to Mr. F. W. Jordan for assistance in carrying out the experiments.

As the results of these experiments seem to justify very completely the use of Callendar's parabolic formula over a wide range, a table has been calculated by which the value of T may be obtained directly from the value of P*t* for a range of temperature extending from -200 to $+1100°$ C., and for the value 1·5 of the constant δ.

A second short table extends this to all values of δ usually met with. It is hoped that this table may be of general use to others who are employing platinum thermometers.

The experiments were carried out at the National Physical Laboratory, and, in conclusion, I wish to thank those members of the staff who have assisted in it.

"The Spectra of Antarian Stars in Relation to the Fluted Spectrum of Titanium." By A. FOWLER, A.R.C.S., F.R.A.S., Assistant Professor of Physics at the Royal College of Science, South Kensington. Communicated by Professor H. L. CALLENDAR, F.R.S. Received February 18,—Read March 3, 1904.

[PLATE 6.]

The distinguishing feature of the spectra of the Antarian Stars* is the system of apparently dark flutings, sharp towards the violet and fading off towards the red end of the spectrum. The principal flutings are well seen in Antares, but they are more strongly developed in the spectra of α Herculis and o Ceti, in which stars additional details are also seen. These flutings have not hitherto received a definite chemical interpretation, and it has been uncertain, owing to the possibly misleading effects of contrast, whether the spectrum was to be regarded as one consisting wholly of absorption flutings fading towards the red, or as one partly consisting of emission flutings fading in the opposite direction.

The purpose of the present communication is to state the nature of the evidence which indicates that the spectrum is essentially an absorption spectrum, and that the chief substance concerned in the production of the flutings is titanium, or possibly a compound of that element with oxygen.

The first indication of this result was the striking general resemblance of the titanium flutings, as seen in photographs recently obtained, with the stellar flutings, both as to relative intensity and apparent position (Plate 6). The interspaces between the flutings, as they appear on a negative, in some cases also strongly recall the corresponding bright spaces in the stellar spectra.

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* Secchi's Type III; Vogel's Class III*a*.

The most extensive series of visual observations of the Antarian stars were made by Vogel* and Dunér† many years ago, and for the part of the spectrum extending from near D to the extreme red, no other measurements have yet been published. For the region more refrangible than D, however, wave-lengths derived from photographs are available, the most complete statements of these being due to Father Sidgreaves‡ and Mr. Stebbings.§ The individual results given by different observers vary considerably: visual observations are difficult, and, in the case of photographs taken with prismatic cameras, errors doubtless arise through the lack of suitable reference lines. There is also some difficulty in deciding where a fluting actually commences. The evidence in favour of a titanium origin for most of the flutings, however, depends on such a large number of coincidences that it is almost independent of a very precise knowledge of wave-lengths.

The flutings in question come out in the arc spectrum of titanium oxide, if the precaution be taken to provide a liberal supply of material and to use a very long arc, taking care also that the image of the "flame" is projected on the slit of the spectroscope. They are also seen in the arc spectrum of the chloride under similar conditions. Numerous lines accompany the flutings produced in this manner and some of the details are consequently masked or not recognized without careful study of the photographs.

So far the flutings have not been very successfully produced in the oxyhydrogen flame; they are visible in the flame spectrum of the fumes from the chloride, but their observation is difficult on account of the bright continuous spectrum.

The best representation of the flutings has been obtained by passing a spark, without jar, through the fumes of oxychloride which rise from the chloride of titanium on exposure to air. Under these circumstances the lines which appear are not numerous, and some of the secondary flutings which are masked by lines in the spectrum of the flame of the arc are readily detected, in spite of the continuous spectrum which is also present. The few lines which do appear in this spectrum are probably low temperature lines which may be found of special importance in the cooler stars.

Photographs have been taken over the region C to K, the instrument employed being one built up on the Littrow principle, having one prism of 60°,|| and a 2-inch objective of 40 inches focal length, giving a linear dispersion from D to K of 5 inches. Wave-lengths were

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* 'Beobachtungen zu Bothkamp,' vol. 1, p. 20, etc.

† 'Sur les Etoiles à Spectres de la Troisième Classe'; "K. Sven. Vet.-Akad. Hand.," vol. 21, No. 2, 1884.

‡ 'Monthly Notices, R.A.S.,' vol. 58, p. 344; vol. 59, p. 509.

§ 'Lick Observatory Circular,' No. 41, May, 1903.

|| Lent by the Government Grant Committee.

determined in the usual manner by micrometric measurements of the photographs, using reference lines of titanium and iron, and calculating by the Cornu-Hartmann formula; though only provisional, they are probably not greatly in error.

It is instructive first to make a comparison between the more conspicuous flutings and those recorded visually in the stars by Vogel and Dunér. Details of the measurements are given in Table I, but reference should also be made to Plate 6, in which Dunér's drawing of the spectrum of α Herculis, as seen with a spectroscope of small dispersion, is compared with a negative of the titanium flutings, as they appear in the "arc" spectrum of titanium oxide.

Table I.—Comparison of Titanium Flutings with Visual Observations of the Spectra of Antarian Stars.

Titanium flutings.		Antarian flutings (more refrangible edge).	
Wave-length.	Visual intensity.	Wave-length.*	Dunér's number.
7055	10	..	Out of range.
..	..	6493	1
6162·5	10	6164	2
..	..	5862	3
5604·5	8	5596	4
5447·0	10	5453	5
5241·0	5	5243	6
5167·5	10	5169	7
4955·1	8	4960	8
4761·6	7	4769	9
4584·3	5	4608	10

It will be seen be seen that eight of the ten bands recorded by Vogel and Dunér agree within the possible limits of error with the flutings of titanium, and it is to be noted also that the only one of the principal titanium flutings which is not represented in the stellar spectrum is out of range in the extreme red. The origin of the two outstanding bands at 5862 and 6493 has not yet been ascertained. There are traces of titanium flutings near their positions, but they seem inadequate to account for two such distinct bands as those drawn

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* The wave-lengths given are the means of Vogel's and Dunér's measurements, corrected to Rowland's scale (Scheiner's 'Astronomical Spectroscopy,' p. 301). For bands 5, 7, 8, 9, 10, the means of the wave-lengths derived from photographs by Lockyer, Pickering, Sidgreaves and Stebbings are respectively 5448, 5165, 4954 4761, and 4584 (see Table II).

Table II.—Comparison of Titanium Flutings with Photographic Spectra of Antarian Stars.

Flutings of Ti (Fowler).*		Flutings in stars (Stebbings).		Flutings in *o* Ceti (Sidgreaves).		Remarks.
λ.	Intensity.	λ mean of five stars.†	*o* Ceti.	λ.	Intensity.	
			4313 ·4			
4352 ·9	3	..	4352 ·7	4352	7	
4395 ·2	3	..	4395 ·0	4395	5	Masked by lines in arc spectrum.
4422 ·0	2	4421 ·5	4421 ·5	4421	4	,, ,, ,,
4437 ·0	3	..	..	..	..	Masked in arc spectrum. Sidgreaves notes a "wide line" at 4436.
4461 ·9	4	..	4462 ·1	4460	6	Head well defined.
4505 ·0	4	..	4504 ·8	4504	6	Head not very well defined. Not recognised in arc spectrum.
4548 ·4	3	..	4547 ·9	4546	5	Head apparently strengthened by a line at 4548 ·9.
4584 ·3	6	4584 ·4	4584 ·1	4583	10	Beginning of Dunér's band 10, λ 4585 Lockyer,‡ 4586 Pickering.§ Head has the appearance of a double line.
4626 ·4	6	4626 ·3	4625 ·8	4625	8	Head well defined, and has the appearance of a double line.
4667 ·8	5	4667 ·6	4668 ·6	4669	9	,, ,, ,, ,, ,, ,,
4714 ·5	3	4714 ·1	4713 ·2	4714	4	Head not sharply defined.
4738 ·0	2	4737 ·1	..	4736	3	Possibly only an ill-defined line which appears in "chloride" spark, but not in the arc.
4761 ·6	7	4761 ·0	4759 ·0	4758	10	Beginning of Dunér's band 9, λ 4763 Lockyer, 4762 Pickering. Head sharply defined, and has the appearance of a double line.
4805 ·6	7	4804 ·6	4803 ·2	4803	6	Head appears as a double line.
4842 ·0	1	..	4841 ·8	4842	8	A feeble brightening seen only in best photographs; it is not the Ti line λ 4841 ·0.
4848 ·6	5	4848 ·4	..	..	..	Head appears as a double line.
4894 ·0	2	..	..	4892	3	Head indefinite.

5002 ·8	4	..	..	4998	9	Head rather indefinite; not clearly distinguished in arc. Lines at 4981 · 9, 4991 · 2, 4999 ·7, 5007 ·4, 5014 ·4.
5050 ·5	2	..	..	5046	6	Head rather indefinite; not clearly distinguished in arc.
				5074	3	
				5098	4	
				5135	3	
5167 ·5	10	5165 ·8	5165 ·9	5162	10	Beginning of Dunér's band 7, λ 5165 Lockyer, 5168 Pickering. Head very sharply defined and perhaps double with 2nd head at 5169 ·8.
5241 ·0	5	..	..	5237	8	Beginning of Dunér's band 6. Begins with a line which is relatively stronger than in the arc spectrum.
5308 ·0	3	..	5307 ·2	5306	7	
5356 ·6	4	..	5357 ·7	5356	6	
5407 ·0	1	..	..	5406	2	
			5438 ·3			
5447 ·0	10	5446 ·8	5446 ·8	5447	10	Beginning of Dunér's band 5, λ 5455 Lockyer, 5445 Pickering. Head very sharply defined.
5497 ·5	5	5496 ·8	5496 ·9	5498	5	Head well defined.
5604 ·5	8	..	..	5597	8	Beginning of Dunér's band 4. There are strong lines near 5598, 5630, 5662, 5708, which, with small dispersion, might appear to be the heads of the adjacent flutings. Among other details within this group, Sidgreaves notes "bands" at 5603 and 5642, and a "wide line" at 5667.
5636 ·3	6					
5668 · 4	5	..	..	5660	7	
5713 ·9	3	..	..	5709	3	
5760 ·9	5	..	..	5756	8	Head well defined } Among the details in this region Sidgreaves notes "bands" at 5761, 5808, and 5845.
5811 ·0	5	..	..	5804	8	" "
5847 ·2	3	..	..	5840	8	" "

* As seen in spark without jar through fumes from titanium chloride; they are also seen in the arc unless otherwise stated.

† α Herculis, ρ Persei, β Pegasi, α Orionis, α Ceti.

‡ 'Phil. Trans.,' A, vol. 186, 1893, p. 702.

§ 'Annals Harv. Coll. Obs.,' vol. 28 Part 1, p. 8.

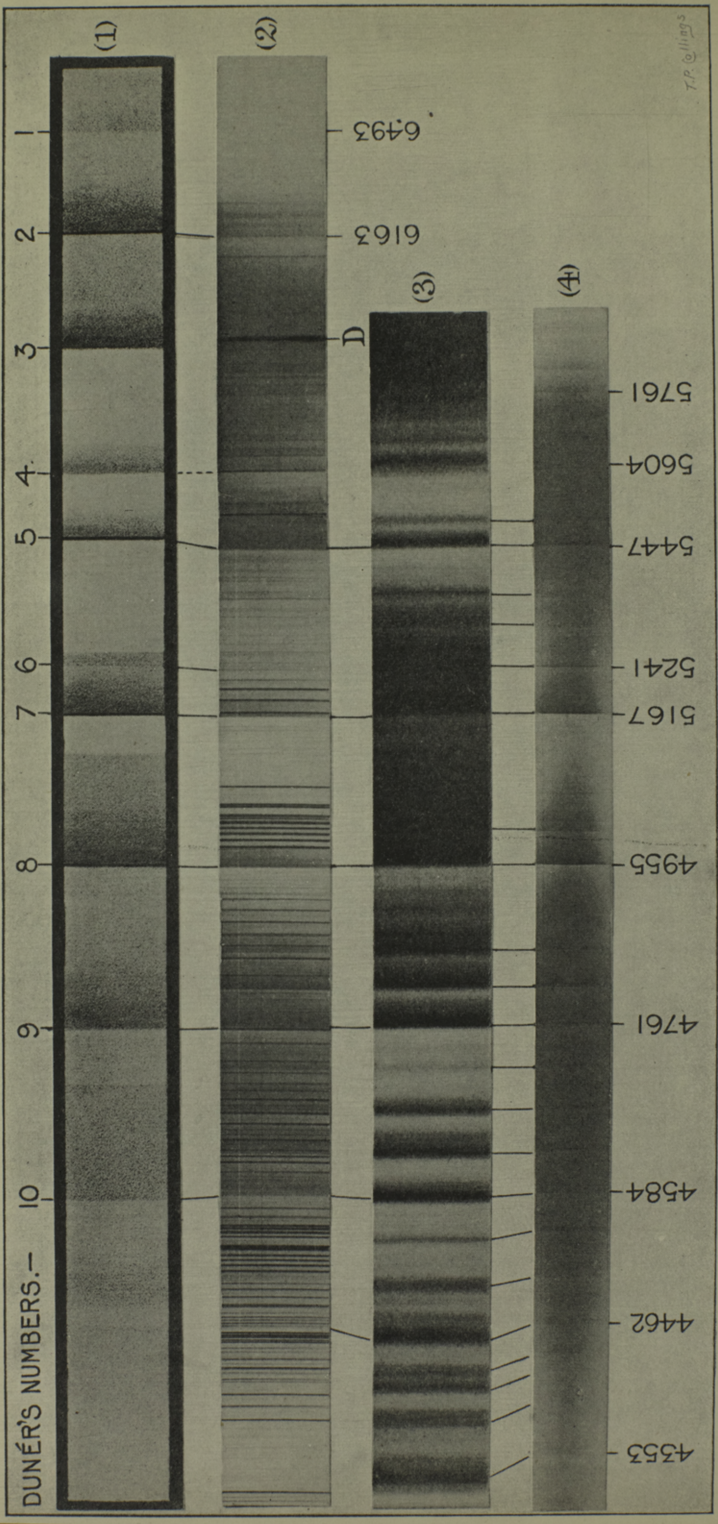
by Dunér. The association of vanadium with titanium in the spectra of sun spots suggested that they might be due to the former element, but this does not appear to be the case. The strongest fluting of vanadium is near 5472, and there is no certain evidence to show the presence of this fluting in the Antarian type of spectrum.

The evidence for titanium in the case of the remaining flutings, however, is enormously strengthened by a discussion of their structure and by extending the comparison further into the violet. Photographs of the stellar spectra, especially those of *o* Ceti and *α* Herculis, show that some of the principal flutings are composite, Dunér's band 10, for example, containing, according to Sidgreaves, four distinct flutings separated by intervals of about 44 tenth-metres, each of which is weaker than the one which precedes it on the more refrangible side. A precisely similar structure is found in the case of the titanium flutings, and a comparison of wave-lengths indicates that the various components occupy the same positions as those in the stars, so far as the available measurements permit the test to be applied. For this comparison (Table II) the wave-lengths derived from photographs by Father Sidgreaves and Mr. Stebbings are utilised. The relation may also be gathered by inspection of the reproductions of the photographs given in Plate 6, that of *o* Ceti having been very kindly placed at my disposal by Father Sidgreaves. Not all the details of the negatives, however, can be brought out in the reproductions, and the relative dispersions are not exactly the same.

It will be seen from the table that the details of the titanium flutings are reproduced with remarkable fidelity in the stellar spectra, and more especially in *o* Ceti. In the latter spectrum the number of flutings recorded is slightly greater than in the case of titanium, but it is by no means certain that every detail of the titanium spectrum has yet been photographed. It is possible also that some of the features described as flutings in the stellar spectrum may be groups of lines, and in at least one instance (4437) a fluting has been classed as a "wide line."

The points of difference are very slight, and are mostly in the less refrangible part of the spectrum, where the reductions of the stellar spectra present the greatest difficulty. There is a peculiar displacement of the fluting 4848 to λ 4842 in the spectrum of *o* Ceti, which may possibly be due to the superposition of a fluting or group of lines of undetermined origin; or, it may be that the feeble maximum observed at 4842 in titanium is strong enough in this spectrum to account for the apparent shift. There is also some uncertainty in connection with the complicated groups of flutings and lines extending from 5598 to D, which need further investigation in the stellar spectra with instruments of greater dispersion.

The general agreement is nevertheless such as to leave no reason-



(1) α Herculis (Dunér). (2) Titanium in flame of arc.
(3) o Ceti (Stonyhurst). (4) Titanium in spark without jar.

ble doubt that titanium is the main factor in the production of the ark flutings which characterise the Antarian group of stars.

This explanation of the dark flutings suggests that the appearance f bright flutings in the Antarian spectrum arises chiefly from effects f contrast. It does not, of course, exclude the possibility of the resence of bright flutings, such as might be indicated by local rightenings which are not exactly in coincidence with the edges of ark flutings.

Whether the absorption flutings are produced by the vapour of tanium or by that of the oxide has not yet been completely etermined. As already pointed out, the flutings may be obtained ther from the oxide or the chloride, but as the latter so readily nites with oxygen on exposure to air, it furnishes no evidence against e supposition that the flutings are due to the oxide.

The author has pleasure in acknowledging the very able assistance hich has been rendered in the experimental work involved in this vestigation by Mr. F. W. Jordan, B.Sc., Teacher in Training in the epartment of Astronomical Physics, Royal College of Science.

DESCRIPTION OF PLATE 6.

Visible spectrum of α Herculis, as drawn by Dunér.

Flutings of titanium, as they appear in the spectrum of the "flame of the arc," when charged with titanium oxide.

Photographic spectrum of *o* Ceti, from a photograph taken at the Stonyhurst College Observatory, November 29, 1897.

Flutings of titanium, as they appear when a spark, without jar, is passed through the fumes which rise from titanium chloride on exposure to air.

(*Note.*—The coincidences cannot be very exactly shown in this manner, on account of the differences of dispersion of the three instruments with which the spectra were recorded.)

III. *The Spectrum of Scandium, and its Relation to Solar Spectra.*

By A. Fowler, *A.R.C.S., F.R.A.S., Assistant Professor of Physics, Imperial College of Science and Technology, South Kensington.*

Communicated by Sir William Crookes, *D.Sc., F.R.S.*

Received June 23,—Read June 25, 1908.

Introductory.

The present investigation of the spectrum of scandium was undertaken in connection with the work on the spectra of sunspots and solar prominences with which I have been occupied during the past few years. The presence of scandium in spots and prominences was already well known, but all the desired information with respect to the positions and characteristics of the various lines could not be gathered from published tables.

Thalén's observations of the spark spectrum[*] extend from 4247 to 6305, but though his intensities give a useful term of comparison in some cases, the wave-lengths lack the precision necessary for use with modern solar tables, and a considerable part of the red is omitted. A few of the Fraunhofer lines were identified with scandium by Rowland,[†] but, probably for want of suitable material for the production of the scandium spectrum, the comparison was far from complete. More extensive observations of the arc and spark spectra have been made by Exner and Haschek,[‡] but, as they extend no further into the visible spectrum than 4744, they scarcely enter the region in which the spectra of spots and prominences are best known. The arc spectrum has been further studied by Lockyer and Baxandall,[§] but here again the region from 5718 to the red end was not included, and but little attempt was made to classify the lines.

Attention was specially drawn to the need for the re-determination of some of Thalén's wave-lengths in the course of a discussion of some observations of the spectra of sunspots in the region C to D,[||] when it was suggested that two very prominent spot lines recorded at 6210·90 and 6306·02 might be due to scandium. THALÉN's wave-lengths for strong scandium lines near these positions were 6210·0 and 6304·0—or 6211·0 and 6305·1 when corrected to ROWLAND's scale—and the identifications seemed probable in consequence of the undoubted presence in spots of the scandium line 5672·05. The wave-length 6306·02 was adopted by Father CORTIE and myself because the spot line could not be distinguished from the telluric oxygen line in that position with the instruments employed, but with greater dispersion MITCHELL* and NEWALL† subsequently identified the spot line with ROWLAND's solar line 6305·88. Observations for checking these identifications were long delayed on account of the difficulty of obtaining a specimen of scandium with which to produce the spectrum, but a few months ago, after an examination of several minerals reputed to contain rare earths, a strong scandium spectrum was obtained from a piece of South African euxenite. The spectrum obtained in this way was admixed with lines and bands of calcium, yttrium, and other substances, but it was quite adequate for the re-determination of wave-lengths, assuming the lines to have been correctly attributed to scandium by THALÉN. Measurements of photographs of the arc spectrum of the mineral removed all doubt as to the precise correspondence of the spot lines 6210·90 and 6305·88 with strong lines of scandium first tabulated by THALÉN.

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[*] 'Watt's Index of Spectra,' p. 125.

[†] 'Preliminary Table of Solar Spectrum Wave-lengths,' Chicago, 1896.

[‡] 'Wellenlängen-Tabellen' (Leipzig und Wien, 1904).

[§] 'Roy. Soc. Proc.,' vol. 74, p. 538 (1905).

[||] 'Monthly Notices, R.A.S.,' vol. 65, p. 211 (1905).

The scandium lines came out so clearly in the spectra of some of the fragments of euxenite that I was induced to carry the inquiry a stage further, in view of the peculiar selection of lines for representation in the solar spectrum and in sunspots. As I have previously remarked :‡ "The scandium lines which appear in the spots are among the strongest in the arc spectrum, while the possible coincidences with the fainter lines are so few as to be probably accidental. At the same time there are some strong arc lines which are not intensified in the spots ; it is a noticeable fact that these are more intense in the solar spectrum than those which appear in the spots, and the probability is that all of them, like 5527·03, are related to the enhanced-line class." There is a similar selection of lines in the chromospheric spectrum, as also remarked by LOCKYER and BAXANDALL, but the lines are different from those which appear in spots.

Similar differences of behaviour have been noted in the case of other elements, but scandium appeared to be rather an extreme example, and further study of the varying intensities of its lines promised to be of value, not only in identifying particular lines with scandium, but in helping to establish the principles to be followed in assigning solar lines of different classes to metallic origins.

On comparing the euxenite spectrum with the scandium arc recorded by LOCKYER and BAXANDALL it was at once evident that the intensities assigned in the two cases were often widely different. For example, the two lines 5527 and 5672 are given as

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* 'Astrophys. Jour.,' vol. 22, p. 27 (1905).

† 'Monthly Notices, R.A.S.,' vol. 67, p. 167 (1906).

‡ 'Trans. Int. Sol. Union,' vol. 1, p. 228 (1906).

10 and 9 respectively in the scandium arc, while in the euxenite arc the former was less than half the intensity of the latter. Such differences as this are no doubt to be accounted for by differences in the conditions of experiment. **Lockyer** and **Baxandall** worked with scandium oxalate, and probably obtained what may be properly considered the arc spectrum of the element. In euxenite, on the other hand, the presence of calcium and other substances tended to produce the condition of a "flaming arc," and the scandium lines doubtless appeared with intensities approximating to those proper to the "arc-flame" or "flame" spectrum. That is, in euxenite the presumably "enhanced lines"* were notably weakened as compared with their intensities in the true arc spectrum. Further evidence that these weakened lines were enhanced lines was given in some cases by comparison with the spark intensities of **Thalén**.

Although a comparison of intensities estimated by different observers is often apt to be misleading, the "inversions" in the case of several scandium lines were sufficiently pronounced to support the previous deduction, from the behaviour of other elements, that flame lines were strengthened and enhanced lines weakened in spots, while the enhanced lines might appear alone in the upper chromosphere.

At this stage of the investigation I was fortunate enough to receive the valuable assistance of Sir **William Crookes**. In reply to an inquiry about two years ago Sir **William Crookes** informed me that scandium was extremely scarce, and that, although he had been carefully collecting residues for some time, he had not then obtained sufficient for a satisfactory examination of the spectrum. By the end of last year, however, when I acquainted him with the results obtained from euxenite, he not only informed me that he had succeeded in collecting and purifying a considerable amount of scandia (Sc_2O_3), but very generously placed half a gramme of the substance at my disposal. It thus became possible to make a much more complete catalogue of scandium lines, and a more satisfactory investigation of the behaviour of the lines under varying experimental conditions. As Sir **William Crookes** was himself occupied with the spark spectrum, the electric arc was exclusively employed in my own work, but the conditions were varied so as to give in some cases an approach to the spark spectrum, and in others to the flame spectrum.

The Spectrograph Employed.

The photographs were taken with a spectrograph of Littrow form, having a lens of 12 feet focal length, and one prism of 60° for which μ_D is 1·6467. The plates are 12 inches in length, and show satisfactory definition throughout, the region covered being 3930 to 4670, or 4670 to 6600, according to the position of the mirror which returns the light through the prism. At 6600 the linear dispersion is 12·7 tenth-metres to the millimetre, while at 3930 it increases to 1·8 tenth-metres per millimetre.

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* "Enhanced lines" are lines which are relatively strengthened in passing from the arc to the spark (**Lockyer**).

The determination of wave-lengths was made in the usual manner with the aid of the Cornu-Hartmann interpolation formula for prismatic spectra, a separate equation being computed for each region of 100 to 200 tenth-metres. Lines in a comparison spectrum of iron, slightly overlapping that of scandium, were used as standards, ROWLAND'S solar wave-lengths for corresponding lines being adopted. Numerous iron lines were included in the measures, and small corrections, depending upon the degree of agreement between the computed and observed values of these extra lines, were applied to the resulting wave-lengths for scandium.

On comparison with LOCKYER and BAXANDALL'S wave-lengths, it was found that there were small systematic differences in some parts of the spectrum which persisted after repeated measurements of different plates. It was accordingly thought desirable to take another photograph in which iron was mixed with scandia, so that there should be no possibility of a relative displacement of the comparison lines. The previously deduced wave-lengths were fully confirmed by this procedure.

For all but the weakest lines it is hoped that in the part of the spectrum more refrangible than D the wave-lengths are correct to within two or three hundredths of a tenth-metre, while on the red side of D, in consequence of the smaller dispersion, the errors may be somewhat greater.

The Arc Spectrum.

The arc spectrum was produced in the ordinary manner by introducing a small quantity of scandia between carbon poles, the current being obtained from the 110-volt lighting circuit. The P.D. between the poles was about 40 volts, and the current 8 amperes. The scandia did not volatilise very readily, and with the small amount of material that one felt justified in using, carbon flutings were also present in the spectrum and tended to conceal some of the fainter metallic lines. Better results were obtained by mixing a little silicate of soda or silicate of potash with the scandia, the carbon flutings being then practically eliminated, and a good spectrum secured with a very small amount of scandia. The few impurity lines introduced in this way were readily recognised, and were less objectionable than the multitude of lines composing the carbon flutings. To avoid unnecessary waste of so rare a substance, the arc was usually enclosed in a glass globe, so that the residues might be collected and the scandia subsequently separated by chemical treatment.

A list of the arc lines between K and C is given in Table I., at the end of this paper. The intensities are on a scale such that 10 corresponds to the brightest lines, and 1 to lines which are just well visible on negatives taken with moderate exposures; very faint lines, which only appeared clearly on strong photographs, are indicated, on ROWLAND'S plan, by 0 and 00. The estimates of intensity are based on an examination of several negatives made with varying exposures, as there is a tendency for small differences in the brighter lines to be effaced by long exposure. It should be understood, however, that the intensities estimated in this way indicate little more than the relative brightnesses of the lines in the same part of the spectrum.

The enhanced lines, of which 5527·0 may be taken as a type, fluctuated considerably in intensity in the arc and appeared differently on different photographs. Nevertheless, all the lines of this class varied together, so that there was no change in the intensities of the enhanced lines with respect to each other, but only with respect to the arc lines.

The flutings which occur in the arc spectrum are dealt with under a separate heading.

The Arc in Hydrogen.

The well-known experiments of Crew* and others† have shown that, when the arc is surrounded by an atmosphere of hydrogen, the spectrum changes in the direction of that given by the spark. Flame lines are relatively reduced and enhanced lines increased in intensity.

Photographs of the scandium arc in hydrogen, at a pressure of about 75 mm., were taken, and the enhanced lines were readily identified by their strengthening when observed in this way. The use of the arc in hydrogen probably does not reveal anything more than the spark as regards the line spectrum, but is sometimes a convenient method of arriving at the same result. Scandia, however, was rather refractory under this treatment, and it was not found possible to avoid the presence of carbon flutings in the photographs.

An interesting result of this experiment was the complete disappearance of the scandium flutings which form such a striking feature of the arc in air.

Although the enhanced lines as a whole were brightened when the arc was passed in hydrogen, their relative intensities were not appreciably different from those found in the ordinary arc. It would therefore serve no useful purpose to give separate estimates of the intensities of the lines in hydrogen. Following Lockyer's notation, the enhanced lines are indicated, in the second column of Table I., by the letter "p" following the intensity number, p being an abbreviation for "proto," so that pSc signifies "protoscandium," and so on.

For the more refrangible part of the spectrum (3930 to 4670) the enhanced lines were identified first by their behaviour in the arc-flame, as explained under the next heading, and checked by reference to a photograph of the spark spectrum which was kindly forwarded to me by Sir William Crookes.

It should be noted that the enhanced lines of scandium differ from those of iron, titanium, and certain other elements, in exhibiting themselves with relatively great intensity in the ordinary arc spectrum, as well as in the spark spectrum. Why this should be so is not quite clear, but scandium is not alone in this behaviour, as reference to the spectra of calcium, strontium, and barium will show, though this point has received little attention hitherto. In the case of the iron arc, the enhanced lines are almost insignificant in the integrated light, but they appear with considerable intensity close to the positive pole, and with less intensity near the negative pole.[*] It would seem that in the case of scandium and the other elements named the region of the arc in which enhanced lines are produced is of greater extent than in the case of such substances as iron. However that may be, the H and K lines of calcium, the lines 4078, 4215 of strontium, the lines 4554, 4934 of barium, and the lines of scandium in question, have all the other characteristics of enhanced lines and may be properly regarded as such. They are weakened in the flame, relatively brightened in the spark, and are isolated from the other lines of the arc spectra when observed in the upper chromosphere and in certain stellar spectra. The enhanced lines are, in fact, to be regarded as forming a distinct spectrum of scandium, which may or may not co-exist with the other lines according to circumstances. A separate list of these lines is given in Table V.

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* 'Astrophys. Jour.,' vol. 12, p. 167 (1900).

† 'Roy. Soc. Proc.,' vol. 72, p. 253 (1903).

The Arc-Flame Spectrum.

An economical method of producing an approximation to the flame spectrum was suggested by the observations of the spectrum of euxenite, to which reference has already been made. It was felt that the material available was inadequate for the effective use of the oxyhydrogen flame, or even for the comparatively long exposures required for the outer part of the flame of an ordinary arc.

The method of purposely introducing other substances into the arc was therefore adopted, the idea being to produce a "flaming arc" without unduly increasing the number of impurity lines in the spectrum. For this purpose silicate of soda, silicate of potash, and sodium chloride were separately tried and found to be effective if used in sufficient quantity. A very long "arc" was thus obtained (the P.D. between the poles falling to about 30 volts), and photographs were secured in which the enhanced lines, including even the strong line 5527, were reduced to mere traces. In the blue end of the spectrum the strong enhanced lines were much enfeebled in other photographs covering this region, and it might have been possible to abolish these lines also if more material had been available for continued experiments.

It should be mentioned that the spectrum fluctuated considerably, the enhanced lines occasionally coming in as in the ordinary arc, but, so far as possible, the exposures were only made in the intervals when visual observations showed that the enhanced lines were absent from the spectrum. The desired condition could be restored, in a general way, by adding more of the supplementary substance.

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[*] FOWLER, 'Monthly Notices R.A.S.,' vol. 67, p. 154 (1906).

A valuable confirmation of the identification of the enhanced lines was thus obtained, but as regards the remaining lines it can only be said that, within the limits of these experiments, the brighter arc lines survived in the "arc-flame" with little change in their relative intensities.

The arc-flame spectrum may accordingly be regarded as consisting of the brighter lines of the arc spectrum, except that the enhanced lines (indicated by "p" in the second column of Table I.) are entirely absent. Separate estimates of intensities in the arc-flame would therefore be superfluous, and might be misleading. The principal lines of the arc-flame spectrum are brought together in Table IV.

Impurities.

Allowing for the impurities known to be introduced by the use of carbon poles, or by admixture with other substances for the special purposes already mentioned, there is no evidence of any considerable impurity in the scandia so carefully prepared by Sir **William Crookes**. In the blue end of the spectrum, thanks chiefly to the admirable work of **Exner** and **Haschek**, fairly complete data are available for the detection of such impurities, and in this region at least, with the exception of the yttrium line 4883·8, all the probable impurity lines are extremely faint. In the less refrangible parts of the spectrum the existing records do not permit the identification of impurities to the same extent, but from the evidence afforded by the blue end it is unlikely that any but very faint lines will turn out to be due to substances other than scandium.

A list of the lines rejected as impurities (excluding those of calcium, barium, iron, sodium, and potassium introduced in the course of the observations) is given in Table II. It will be seen that the principal impurity lines are attributed to yttrium, ytterbium, thorium, and cerium, while a few lines are probably due to samarium, gadolinium, and europium. Other faint lines at present included in the general list of scandium lines, Table I., may subsequently have to be rejected as impurity lines, more especially those which occur in the region less refrangible than 4700.

As will be seen from Table I., not more than two of the lines given by **Exner** and **Haschek** do not occur in Sir **William Crookes**' scandia, while several of **Lockyer** and **Baxandall**'s lines have not been found. The scandium oxalate with which the latter observers worked was admittedly impure, and it would appear probable that lines given by them which do not occur in my own list are not due to scandium. As no list of rejected lines was given by **Lockyer** and **Baxandall**, it cannot be determined to what extent the additional lines in my table should be attributed to impurities on similar grounds.

As already remarked, impurity lines in my own catalogue are probably only to be expected among those of very low intensity, but several well-marked lines are not recorded by **Lockyer** and **Baxandall**. In reply to an inquiry as to three of these lines, 5210·7, 5219·7, and 5375·5, all of which were given as scandium lines by Thalén, Sir Norman Lockyer has kindly informed me that weak lines in these positions were found on the Kensington photographs, but not included in the published list. The line at 5210·7 was almost masked by the shading from the strong silver line 5209·6 arising from the silver poles employed for the arc, and this probably accounts for its being passed over. In the case of 5219·7 the line was marked on the photograph as an impurity, but the record as to the substance to which it was attributed has been misplaced. The third line, 5375·5, was omitted as being possibly due to thorium, for which Thalén gives a fairly strong line at 5374·6, or 5375·6 when corrected to Rowland's scale. A photograph of the thorium spectrum, taken for the purpose, shows that the line in question is not truly coincident with the thorium line. There accordingly seems to be no sufficient reason why these three lines should not be regarded as part of the scandium spectrum.

Flutings.

In addition to the line spectrum, all the photographs, with the exception of those of the arc in hydrogen, show a fluted spectrum which is especially strong towards the red end, but extends also into the green and blue-green. Several of these flutings have previously been noted in the spark spectrum by Thalén, who regarded them as being probably due to the oxide of scandium and not to the metal itself. The complete disappearance of the flutings when the arc is passed in hydrogen tends to confirm Thalén's view that they originate in the oxide, but no further research on this point has yet been undertaken.

A list of the flutings, all of which fade away towards the red, is given in Table III. An attempt has been made to include all the fainter heads as well as the bright ones, but some of the heads are rather diffuse and the positions consequently somewhat uncertain.

By far the brightest group of flutings is in the orange-red, beginning at 6017·3, and there are fainter groups beginning at 6408·7 and 5737·2. There are no flutings in the middle green, but three rather feeble flutings, showing structure lines over a long range, begin at 4672·8, 4858·2, and 5133·8. No flutings have been found in the blue and violet.

In the sunspot spectrum there is a hazy line about 6036·6 which may perhaps correspond with the brightest scandium fluting measured as 6036·48, but as the other bright heads cannot certainly be traced (partly on account of Fraunhofer lines) the evidence as to the presence of scandium oxide in spots is very slight.

Comparison with the Solar Spectrum.

Several important additions to Rowland's identifications of solar lines with scandium were made by Lockyer and Baxandall, and other possible coincidences were indicated. The intensities of the solar lines, however, were often disproportionate to those of corresponding lines in the arc spectrum.

If we dealt only with the arc spectrum of the element in relation to the sun, the selection of lines for representation in the Fraunhofer spectrum would certainly be very remarkable. Of two lines in the same part of the spectrum one may be a comparatively strong line in the sun, while the other, although at least equally strong in the arc, may be weak or missing. For example, the strong line 5672 only occurs with intensity 0 in the sun, while 5684, which is much weaker in the arc, appears with intensity 1 in the sun.

These differences, however, become comprehensible when due attention is given to the properties of the different lines. The lines of scandium which appear most prominently among the Fraunhofer lines are, in fact, the enhanced lines, and within the limits of error of estimation they appear with relative intensities which are identical with those in the terrestrial spectrum. Lines other than those which are enhanced, even though strong lines in the arc, occur only as very faint lines in the solar spectrum.

The coincidences between scandium and solar lines, within the limits of error, are numerous, but many of them cannot reasonably be regarded as other than accidental. Even a faint solar line may properly be attributed to scandium if coincident with an enhanced line of corresponding intensity; but if the scandium line be not an enhanced one, the coincidence can only be accepted as significant when the solar line is faint and the scandium line strong.

The solar lines which may be regarded as true identifications with scandium, in accordance with this conclusion, are indicated in Tables IV. and V., one showing coincidences with arc-flame lines, and the other with enhanced lines. It will be seen that, notwithstanding the occasional confusion caused by lines of other elements, the stronger lines of the arc-flame are represented as consistently as can be expected when dealing with very faint lines appearing in such a complex spectrum as that of the sun. The identification of the enhanced lines, as shown in Table V., is much more definite, in consequence of the greater intensities of the corresponding solar lines.

The result of this comparison is of further interest in relation to the structure of the reversing layer. It has already been suggested by JEWELL,[*] MITCHELL,[†] and others, that different Fraunhofer lines are produced at different levels, and the discussion of the scandium lines tends to support this view. In the case of iron all the arc lines, down to the faintest, are well represented by dark lines in the sun, and there are no enhanced lines so strongly shown as the stronger arc lines. With scandium it is just the opposite, and the simplest supposition to make is that only a small amount of scandium absorption originates at the level which produces the majority of the Fraunhofer iron lines. Since direct observations show that enhanced lines, both of scandium and iron, occur in the upper chromosphere (see p. 59), it seems to follow that the greater part of the scandium absorption is produced at a relatively high level, where the conditions are such as to bring about the comparative isolation of the enhanced lines. The same is probably true of strontium and barium, where the enhanced lines are strong in the Fraunhofer spectrum, and in the upper chromosphere, while the arc lines are feeble or missing.

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[*] 'Astrophys. Jour.,' vol. 4, p. 138 (1896).

[†] 'Astrophys. Jour.,' vol. 22, p. 37 (1905).

It results that while in the case of some elements solar identifications are to be based chiefly on arc lines, in others it is the enhanced lines which may be expected to show the most important coincidences.

Comparison with the Sunspot Spectrum.

The previous work of HALE[*] and myself[†] has shown that in the spectra of sunspots there is a general tendency for Fraunhofer lines of enhanced metallic origins to be weakened, while flame lines are specially selected for strengthening. This difference of behaviour is well marked in the case of scandium, as will be seen from Tables IV. and V. The data for spots given under "HALE" are derived from the Mount Wilson preliminary catalogue of spot lines, extending from 5009 to 5853,[‡] and from the recent more detailed list covering the region 4000 to 4500.[§] The intensities under my own name have been derived either from the Mount Wilson photographic map of the spot spectrum (4600 to 7200), or from photographs in the region 3930 to 5800 which have been kindly placed at my disposal by Mr. MICHIE SMITH, Director of the Kodaikanal Observatory, India. Several lines which have escaped record in the published catalogues of spot lines are clearly seen to be affected when special attention is directed to them. Some of the lines have also been noted in my own visual observations, and in those of CORTIE and MITCHELL.

Referring first to the enhanced lines of scandium (Table V.), it is evident that in the less refrangible parts of the spectrum there is a distinct weakening of these lines in spots, while in the region more refrangible than F the evidence as to actual weakening is very slight. For the most part there is no definite change of intensity of the enhanced lines in the blue end of the spectrum, but it has already been recognised that, on account of photospheric light diffused over the spot, or from still undetermined causes, the sunspot spectrum as a whole tends to lose its characteristic features in the blue and violet, in so far as it has yet been photographically registered.[‖] If the difference in the two parts of the spectrum be real, and independent of the conditions of observation, it may be that the phenomenon is related to that found in some of the Wolf-Rayet stars, where the less refrangible lines of hydrogen are bright and the more refrangible ones dark.*

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[*] 'Astrophys. Jour.,' vol. 24, p. 202 (1906).

[†] 'Trans. Int. Sol. Union,' vol. 1, p. 228 (1906).

[‡] 'Astrophys. Jour.,' vol. 23, p. 15 (1906).

[§] 'Astrophys. Jour.,' vol. 27, p. 45 (1908).

[‖] HALE, 'Astrophys. Jour.,' vol. 25, p. 90 (1907).

A general comparison of the unenhanced lines with the spot spectrum shows that all the more prominent lines are considerably strengthened in passing from the sun to the spot. Seeing that the spot spectrum is far more crowded with lines and flutings than the solar spectrum, it is not surprising that there are several apparent coincidences of spot lines with the fainter lines of scandium, but, with our present knowledge, it would be unphilosophical to regard such occasional coincidences as significant. The only scandium lines which can confidently be regarded as intensified in the spot spectrum are, in fact, those which are brightest in the arc-flame spectrum previously described. The strongest line of all is 6305·88, and other prominent lines are 6210·90, 5700·40, 5687·05, and 5672·05; in the blue end, the strengthening of arc-flame lines, like the weakening of enhanced lines, is less marked in the photographs at present available.

The principal lines of the arc-flame spectrum, including all the unenhanced lines of intensity 6 or more from Table I., are brought together in Table IV. and compared with the sun and sunspots. There is a certain amount of confusion with lines of other elements in spots, but it may be reasonably concluded that the intensities of the lines in spots correspond closely with their intensities in the arc-flame. The line 5514·44 does not appear in the spot spectrum as might have been expected, but it is at the lower limit of intensity, and it would be unwise to conclude from the behaviour of a single line that the conditions in spots are very different from those of the arc-flame. It may be supposed that while there is a general increase in the scandium flame absorption, the increase does not suffice to bring the fainter lines to an intensity within the range of observation.

It is quite certain, therefore, that while the enhanced lines of scandium are weakened in spots, the remaining lines are strengthened more or less in proportion to their intensities in the arc-flame, at least in the less refrangible parts of the spectrum. As the relative intensities of the two sets of lines in spots approximate to those found in the arc spectrum, it is possible that there is a descent of scandium vapour from the upper region, where the conditions are such as to produce enhanced lines, to a lower level where the prevailing conditions approximate to those of the arc. Reduced temperature of the spot vapour, accompanying this change of level, perhaps provides the readiest explanation of the difference between the Fraunhofer and spot spectrum, but much further investigation in several directions is necessary before the precise nature of the action in spots can be ascertained.

Comparison with the Chromosphere.

Two principal sources of data relating to the chromosphere are available for comparison with terrestrial spectra: namely, eclipse photographs, and visual observations made at ordinary times, the former being especially valuable for the blue end, and the latter for the less refrangible parts of the spectrum. Eclipse records are now numerous, but completely satisfactory discussions of the lines are not yet possible, owing to discordances in the wave-lengths given by different observers, and the inadequate resolving powers of most of the instruments which have been employed. Nevertheless, since identifications usually depend upon apparent agreement in wave-lengths and intensities of several lines of the same substance, there is reasonable certainty as to the origins of many of the lines.

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* Campbell, 'Ast. and Astrophysics,' vol. 13, p. 457 (1894).

YOUNG's well-known catalogue of chromospheric lines,* observed without eclipse, remains the principal source of information with regard to the less refrangible parts of the spectrum, though supplementary observations have been made by MITCHELL,† NAGARAJA,‡ and myself.§ Further determinations of the wave-lengths and characters of many of the chromospheric lines, however, are urgently needed. YOUNG's observations were mostly made before ROWLAND's photographic map of the solar spectrum became available, and his subsequent revision was only fragmentary, so that many of the wave-lengths cannot be regarded as final. A more complete distinction between "high-level" and "low-level" lines is also greatly to be desired.

A few lines of scandium have been noted by LOCKYER and others in eclipse spectra, and a greater number by DYSON,‖ who pointed out that the intensities agree well with those of the spark. Making due allowance for the lack of highly precise data, the general result of the more complete comparison which is now possible is to show that it is only the enhanced lines of this element which can be regarded as contributing to the chromospheric spectrum. Of the four strongest lines of the arc-flame spectrum, 6305·88, 5672·05, 4023·83, and 4020·55, there is no suggestion of a chromospheric coincidence except in the case of the last; DYSON gives a line at 4020·50 in his eclipse list, but, as there is no indication of the adjacent similar line at 4023, the coincidence may be considered accidental, especially as the wave-length given by EVERSHED¶ is 4020·3.

A complete list of the enhanced lines of scandium is given in Table V., which also shows the corresponding solar and chromospheric lines. For the region more refrangible than 4670, the latter have been taken from DYSON's tables, while the less refrangible lines, with their "frequencies" and brightnesses, are from YOUNG's catalogue. All the brighter enhanced lines are obviously present in the chromosphere, but the fainter ones, as might be expected, have not yet been recorded.

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[*] SCHEINER's 'Astronomical Spectroscopy,' FROST's translation, pp. 184 and 423.

[†] 'Astrophys. Jour.,' vol. 24, p. 82 (1906).

[‡] 'Astrophys. Jour.,' vol. 26, p. 150 (1907).

[§] 'Monthly Not. R.A.S.,' vol. 66, p. 362 (1906).

[‖] 'Phil. Trans.,' A, vol. 206, p. 440 (1906).

[¶] 'Phil. Trans.,' A, vol. 201, p. 487 (1903).

Apart from the interference of other lines, the intensities correspond closely with those of the terrestrial spectrum.

This result is in good accordance with the work of **Lockyer** on eclipse spectra, which has shown that enhanced lines in general are specially developed in the chromosphere. My own observations* have further shown that enhanced lines appear as "high-level" lines in the chromosphere, while arc lines are mostly restricted to the region near the photosphere. In the case of scandium, the enhanced line 5527 is certainly a high-level line, and 5240, according to my recent observations, is of the same type. That the same is true of other enhanced lines in the blue, notably 4247, is indicated by the lengths of the corresponding arcs in photographs of eclipses taken with the prismatic camera. In **Young's** catalogue high frequency may often be taken as an indication of high level, since lines of the latter class are brought into view by comparatively feeble disturbances, and the lines 5031, 5658, and 5684 may be regarded as of the high-level class from this evidence.

It may therefore be concluded that scandium exists in the higher reaches of the chromosphere, under conditions specially favourable to the production of enhanced lines, while there is no evidence of its presence at lower levels except that afforded by the feebly developed arc lines in the Fraunhofer spectrum.

Summary of Results.

1. The arc spectrum of scandium consists of two distinct sets of lines, which behave very differently in solar spectra. Each set includes both strong and faint lines.

2. Lines belonging to one set correspond with the enhanced lines of other elements, notwithstanding that they appear strongly in the ordinary arc spectrum.

   (*a*) These lines are very feeble or missing from the arc-flame spectrum, and are strengthened in passing to the arc, the arc in hydrogen, or the spark.
   (*b*) They occur as relatively strong lines in the Fraunhofer spectrum.
   (*c*) They are weakened in the sun-spot spectrum.
   (*d*) They occur as high-level lines in the chromosphere.

3. The remaining lines show a great contrast when compared with the first group.

   (*a*) They are relatively strong lines in the arc-flame.
   (*b*) They are very feebly represented in the Fraunhofer spectrum.
   (*c*) The stronger lines are prominent in sun-spot spectra.
   (*d*) They have not been recorded in the spectrum of the chromosphere.

4. The special development of the enhanced lines in the Fraunhofer spectrum, together with their presence in the upper chromosphere, indicates that the greater

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* 'Monthly Not. R.A.S.,' vol. 66, p. 362 (1906).

part of the scandium absorption in the solar spectrum originates at a higher level than that at which the greater part of the iron absorption is produced.

5. The discussion of scandium lines indicates that while in the case of some elements solar identifications are to be based chiefly on arc lines, in others it is the enhanced lines which may be expected to show the most important coincidences.

6. The flutings which occur in the arc and arc-flame spectra do not appear when the arc is passed in an atmosphere of hydrogen. As suggested by THALÉN, they are probably due to oxide of scandium.

In concluding this paper the author is anxious to express his great indebtedness to Sir WILLIAM CROOKES, without whose aid in providing purified scandia the greater part of the investigation would not have been possible. Valuable assistance in taking the photographs, and in checking some of the determinations of wave-lengths, has also been rendered by Miss L. ALCOCK, A.R.C.S., B.Sc., H. SHAW, A.R.C.S., and A. EAGLE, A.R.C.S.

TABLE I.—Arc Spectrum of Scandium.

FOWLER.		LOCKYER and BAXANDALL.		EXNER and HASCHEK.		Remarks.
Wave-length.	Intensity.	Wave-length.	Intensity.	Wave-length.	Intensity.	
3933·55	3	*		3933·59	6	* Possibly masked by Ca line.
	*			52·43	1	* Photographs rather weak here.
89·18	0			89·18	1	
96·76	6	3996·75	5	96·79	15	ROWLAND gives Sc in sun at 96·68.
4014·65	2p*	4014·66	3	4014·68	6	* Lines marked "p" are enhanced lines.
20·55	9	20·55	8	20·60	20	Strong arc-flame line.
23·40	0			23·36	1	
23·83	10	23·88	8	23·88	30	Strongest line of arc-flame spectrum in blue.
31·53	1			31·51	2	
34·37	0			34·35	2	
37·00	0			36·98	1	
43·98	2			43·97	2	
46·64	1			46·64	2	
47·96	4	47·97	4–5	47·98	10	
50·11	1			50·09	2	
52·00	0			52·00	1	
54·71	6	54·68	3	54·71	10	
56·75	2			56·72	3	
67·17	1			67·15	2	
75·13	1			75·13	2	
78·72	1			78·70	2	
82·59	7	82·59	6	82·60	15	Strong arc-flame line.
86·20	0			86·15	1	
		86·67	2–3			

Table I (continued).

Fowler.		Lockyer and Baxandall.		Exner and Haschek.		Remarks.
Wave-length.	Intensity.	Wave-length.	Intensity.	Wave-length.	Intensity.	
4086·81	1			4086·80	3	La ?
87·29	2	4087·26	1	87·28	3	
		94·85	2–3			
95·01	1			95·03	1	
		4106·02	2–3			
4133·18	3	33·10	2	4133·10	4	
40·45	4	40·42	2–3	40·42	5	
		41·78	1			
52·52	4	52·50	3	52·51	8	
		62·85	1			
		63·77	1			
65·37	4	65·38	2–3	65·39	8	
		71·47	1–2			
71·93	2	71·98	2–3	71·92	2	
4218·41	0			4218·43	1	
19·90	0			19·90	1	
22·07	0					
		4224·32	1			
25·78	1			25·76	1	
32·09	2			32·13	1	
33·80	2			33·83	2	
37·94	0			37·96	1	
38·25	3	38·25	2	38·21	3	
39·74	0			39·72	1	
46·30	0			46·27	1	
47·00	10p	47·00	10	47·02	50	Strongest enhanced line in blue.
				51·22	1	
59·86	0					
83·74	1			83·71	1	
86·73	1			86·71	1	Er ?
94·94	4p	94·91	4–5	94·94	5	
4305·88	4p	4305·83	4–5	4305·89	8	
14·25	7p	14·25	9	14·31	30	Strong enhanced triplet.
20·91	7p	20·90	9	20·98	20	
25·15	6p	25·15	8	25·22	20	
48·66	0					
54·78	4p	54·74	3–4	54·79	3	
58·85	1			58·85	1	
59·23	1			59·25	1	
59·83	0					
65·11	1					
74·68	8p	74·65	8	74·69	20	Strong enhanced line.
75·34	0			75·32	1	
81·43	1					
84·97	3p	84·99	4	84·98	3	
89·75	1			89·76	1	
4400·56	8p	4400·56	8	4400·63	20	Strong enhanced line.
15·72	7p	15·72	7	15·78	20	,, ,,
20·83	1p	20·82	1–2	20·84	1	
29·08	0					

TABLE I. (continued).

FOWLER.		LOCKYER and BAXANDALL.		EXNER and HASCHEK.		Remarks.
Wave-length.	Intensity.	Wave-length.	Intensity.	Wave-length.	Intensity.	
4431·53	1p	4431·56	2–3	4431·52	2	
4542·76	1			4542·74	1	
44·88	2			44·86	1	
57·42	2			57·45	1	
		4563·40	2			
74·20	2			74·20	2	
79·15	1					
4604·94	1			4604·88	1	
09·71	0					
10·16	0					
10·59	0					
70·59	6p	4670·59	7	70·59	5	
80·68	2					
82·16	0					
4707·10	2					
09·51	2			4709·53	1	
11·90	0					
14·03	1					
14·52	1					Ce ?
16·44	1					
17·21	0					
19·48	1					
20·95	0					
28·95	2			29·00	1	
29·39	5	4729·39	3	29·43	2	
32·46	1					
34·28	5	34·31	3–4	34·31	3	
35·27	1					
37·82	6	37·88	4	37·86	3	
41·20	7	41·24	5	41·23	4	
43·98	8	44·04	6	44·01	5	
46·32	1					
49·15	1			(Record	ends.)	
				THALÉN (spark).*		
53·35	6			4753·8	1	
59·11	1					
63·25	3					
71·60	1					
79·53	6					
83·69	0					
84·46	0					
91·69	2					
93·14	0					
		4820·52	2–3			

* Corrected to ROWLAND'S scale.

TABLE I. (continued).

FOWLER.		LOCKYER and BAXANDALL.		THALÉN (spark).		Remarks.
Wave-length.	Intensity.	Wave-length.	Intensity.	Wave-length.	Intensity.	
4821·65	0					
27·47	4			4827·8	1	
33·85	4			33·8	1	
		4837·27	2–3			
39·63	4			38·8	1	
40·62	0					
41·00	0					
47·84	3					
52·86	4					
59·35	0					
64·95	1					
75·50	0					
78·36	2					Not Ca 78·31 or Fe 78·41.
80·90	1					
90·55	1					
93·15	1					
4906·88	2					
09·89	3			4909·5	1	
23·00	2			22·5	1	
34·39	1					Not Ba 34·24.
35·95	1					Yb ?
		4937·29	2–3			
41·49	2					
51·46	1					Er ?
54·22	4	54·12	1–2	54·5	1	
73·82	3			73·9	1	
80·50	4	80·49	1	80·4	1	
83·59	2					
		87·26	1–2			
92·07	4	92·06	1–2	91·8	1	
95·18	1					
		5009·68	2			
5014·32	1					
18·59	2					
20·30	2					
21·67	2					
31·20	6p	31·20	8	5031·1	10	Strong enhanced line.
32·88	1					
64·50	3	64·35	2	64·1	2	
68·98	1					
70·39	4	70·34	3–4	70·6	4	
75·99	3	75·85	1–2	76·1	1	
		79·79	1			
80·26	0					
81·75	8	81·68	6	81·6	6	} Strong arc-flame lines.
83·88	7	83·77	5	83·6	5	
85·71	5	85·64	4	85·6	4	
87·17	7 {	87·06 87·18	3 2	} 87·0	5	
90·07	3	89·95	2	90·1	1	

TABLE I. (continued).

Fowler.		Lockyer and Baxandall.		Thalén (spark).		Remarks.
Wave-length.	Intensity.	Wave-length.	Intensity.	Wave-length.	Intensity.	
5092·54	0					
96·90	3	5096·81	2	5097·0	1	
99·38	4	99·28	3–4	99·1	4	
5101·26	3	5101·21	2	5101·1	1	
		04·43	1			
		05·60	2–3			
09·20	2	09·09	1			
		10·85	<1			
13·00	2	12·87	1			
16·86	3	16·73	2	17·6	2	
		21·60	1			
		31·14	<1			
		47·08	2			
		48·28	2			
5210·68	5			5210·8	2	
11·48	0					
19·06	0					
19·75	5			19·3	2	
39·99	5p	5239·99	5–6	39·8	8	Strong enhanced line.
58·49	5	58·46	2–3	58·3	4	
		69·65	1–2			
85·15	1					
85·90	5	85·88	2	85·5	4	
5302·12	2					
		5307·83	1			
14·91	1					
15·77	1					
18·52	2p	18·41	2	5318·3	2	
23·26	0					
23·94	0					
		25·14	2			
		28·05	1			
31·98	1					
34·43	0					Yb ?
39·58	2			40·0	1	
41·21	2			41·0	1	
43·13	2			42·5	1	
49·47	5	49·32	3	49·5	6	
49·91	2					
50·44	1					
56·26	6	56·14	3–4	56·0	6	
57·38	0					
		58·69	2–3			
75·55	5			75·6	4	Not Th.
		89·89	1–2			
92·30	6	92·12	3	92·5	6	
5416·43	3					
25·80	3					
29·62	3					
33·43	4					

Table I. (continued).

Fowler.		Lockyer and Baxandall.		Thalén (spark).		Remarks.
Wave-length.	Intensity.	Wave-length.	Intensity.	Wave-length.	Intensity.	
5438·54	1					
39·26	2					
42·84	3					
46·37	5			5446·5	4	
47·66	0					
51·58	4			52·0	1	
55·51	2					
65·40	1					
68·64	4					
72·42	4					
74·92	1					
		5478·66	2			
82·20	6	82·18	4	82·1	6	
84·83	6	84·81	3–4	85·1	6	
5514·44	6	5514·40	4	5514·6	6	
20·73	7	20·70	4–5	20·7	6	
27·03	10p	27·03	10	27·2	12	Strongest enhanced line in green.
36·60	2					
41·28	4					
46·63	1					
49·90	0					
50·64	0					
52·05	1					
53·84	2					
61·34	0					
65·06	3			65·2	2	
71·48	0					
79·96	0					
91·58	3	91·44	2	91·7	2	
93·60	2					
5604·40	2					
10·33	1					
24·08	2					
31·24	1					
35·10	0					Not carbon.
41·21	4p			5641·2	6	
46·60	1					
47·78	0					
49·80	2					
58·10	7p	5658·10	7	57·7	8	Strong enhanced line.
58·56	2p	58·56	3–4			
61·86	0					
67·40	3p	67·40	3–4	67·0	4	
69·28	4p	69·25	4	68·8	4	
72·05	10	72·05	9	72·3	8	Strong arc-flame line.
80·38	0					
84·43	5p	84·44	4	84·5	4	
87·05	9	87·07	8	87·3	8	Strong arc-flame line.
91·55	0					
5700·40	8	5700·38	7	5700·8	8	Strong arc-flame line.

TABLE I. (continued).

FOWLER.		LOCKYER and BAXANDALL.		THALÉN (spark).		Remarks.
Wave-length.	Intensity.	Wave-length.	Intensity.	Wave-length.	Intensity.	
5708·85	5			5708·8	4	
11·97	8	5711·98	6	11·8	4	Strong arc-flame line
17·51	5	17·54	3	17·3	4	
21·20	0	(Record	ends			
24·30	5	here.	)	24·8	4	
35·40	0					
39·53	0					
41·56	1					
5894·83	2					
5919·21	3					
31·35	2					
40·70	2					
52·42	3					
61·65	3					
68·44	4					
69·37	4					
88·60	4					
6021·92	0					
26·36	3					
49·02	1					
6146·50	3					
93·94	3					
98·68	2					
6210·90	7			6211·0	8	Strong arc-flame line.
39·95	7			39·1	6	,, ,,
45·85	4p			47·1	6	Strongest enhanced line in red.
50·16	3					
59·15	6			59·1	2	
62·48	3					
73·37	0					
76·47	3					
79·95	3p			80·1	2	
84·66	3					Probably double.
93·24	2					
98·00	0					
6300·85	1p					
05·88	10			6305·1	10	Strongest arc-flame line.
10·15	2p					
21·06	2p					
22·96	0					
45·04	1					
79·02	6					
6413·54	6					
48·42	1					
86·56	0					
95·53	1					
6525·84	3					
58·28	3					

TABLE II.—Impurity Lines omitted from Table I.

Wave-length.	Intensity.	Probable origin.	Wave-length.	Intensity.	Probable origin.
3988·10	00	Yb	4306·87	00	Ce
4077·52	0	Y	4309·81	0	Y
4143·01	0	Y	4352·30	0	Sa
4205·20	0	Eu	4364·82	0	Ce
4222·77	00	Ce	4375·10	0	Y
4231·83	0	U, Zr	4382·03	0	Th
4235·49	0	Mn	4391·30	0	Th
4248·82	0	Ce	4391·85	0	Ce
4270·90	0	Ce	4398·17	0	Y
4280·09	0	Sa	4863·36	0	Th
4282·25	0	Th	4883·86	2	Y
4290·12	0	Ce	4920·00	0	Th
4296·89	0	Ce	5402·94	0	Y
4306·46	00	Gd	5477·86	0	Yb

TABLE III.—Flutings occurring in the Arc Spectrum of Scandium Oxide. (All fade away towards the red.)

FOWLER.		THALÉN.*		Remarks.
Wave-length.	Intensity.	Wave-length.	Intensity.	
4672·85	3			Head of blue fluting } Structure traced to 4850.
4707·10	2			Probable sub-head
4858·25	4			Head of blue-green fluting } Structure traced to 5000.
4893·15	2			Sub-head
5133·86	2			Head of green fluting } Structure traced to 5300.
5171·30	1			Sub-head
5737·20	2	5737·5		Beginning of yellow group.
5761·35	1			
5764·70	2			
5773·10	3	} 5773·0		
5775·55	3			
5797·75	2			
5801·70	2	5802·4		Wide head line.
5810·15	3	} 5810·0		
5811·82	3			
5836·75	2			
5839·90	2	5843·0		Wide head line.
5848·00	3	} 5849·5		
5849·40	3			
5876·95	1			

* Corrected to ROWLAND'S scale.

TABLE III. (continued).

Fowler.		Thalén.*		Remarks.
Wave-length.	Intensity.	Wave-length.	Intensity.	
5878·15	2	5878·0		Wide head line.
5887·90	3	5887·5		" "
5918·30	3	5919·0		" "
5928·20	3			
5959·30	1			Wide head line.
5968·90	2			Confused with adjacent Sc lines in some photos.
6002·58	1			
6017·32	4	6017·0	4	Beginning of orange group.
6036·48	10	6038·0	10	
6055·40	2			
6064·54	9	6065·1	8	
6072·90	8	6072·6	8	
6079·60	8	6080·1	10	
6092·70	1			
6102·07	6	6101·5	6	
6110·17	5			
6116·31	6	6115·9	8	
6140·60	5	6141·1	4	Wide head line. λ rather uncertain.
6148·93	3	6146·1	2	
6154·27	4	6154·1	6	Wide head line.
6180·71	3			" "
6188·35	2			
6193·20	4	6193·4	2	Wide head line.
6220·55	3			
6229·70	2			
6233·30	2			
6408·7	2			Beginning of red group.
6420·2	1			
6437·4	1			
6446·8	2			
6458·2	1–2			
6477·0	1–2			
6485·8	3			
6496·5	1			
6517·8	1			
6526·1	2			
6535·7	2			
6567·3	1			
6576·2	1			

* Corrected to ROWLAND'S scale.

Table IV.—Principal Arc-Flame Lines of Scandium compared with Sun and Sunspots.

Sc arc flame.		Sun (Rowland).		Sunspots.		Remarks.
Wave-length.	Intensity.	Wave-length and origin.	Intensity.	Hale.	Fowler.	
3996·76	6	– 96·75*	00		0	* Rowland attributes 96·68 (00) to Sc.
4020·55	9	Sc 20·55	1	(+Fe) 3	*	* Fe 20·64 strengthened on violet side.
4023·83	10	Sc 23·83	2	3	3–4	
4054·71	6	Sc 54·71	00	*	2	* Close double with Zr 54·59 (0). Strengthened on red side.
4082·59	7	$\left\{\begin{matrix}\text{Sc}\\ \text{Fe}\\ \text{Ti}\end{matrix}\right\}$ 82·59	3	4	4	Compound line in sun and spot.
4737·82	6	Fe ? 37·82	1		2–3*	* Probably not wholly Sc.
4741·20	7	Fe ? 41·26	1		2–3*	* ” ” ”
4743·98	8	– 44·01	000		1	
4753·35	6				0	
4779·53	6				*	* Fe 79·63 strengthened on violet side.
5081·75	8	– 81·76	000	00	0	
5083·88	7	– 83·88	000	00	0	
5087·17	7				*	* Ti 87·24 strengthened on violet side.
5356·26	6	– 56·27	000	00	0	
5392·30	6				0	
5482·20	6	– 82·20	0000		1–2*	* Combined with Ti 82·08.
5484·83	6	– 84·85	000	00–0	0	
5514·44	6	– 14·43	0000			
5520·73	7	– 20·73	00	1	1	
5672·05	10	Sc 72·05	0	2	2	
5687·05	9	– 87·06	000	1–2	1–2	
5700·40	8	– 00·40	00	2–3*	2–3*	* H gives Cu ? 00·51 as spot line, but Sc line is included and is the more affected of the pair.
5711·97	8				*	* Fe 12·10 strengthened on violet side.
6210·90	7	– 10·90	00		4	
6239·95	7	– 39·98	0000		2*	* Partly masked by band lines.
6259·15	6	– 59·14	0000		2	
6305·88	10	– 05·88	0000		6	
6379·02	6				2–3	Falls on band of calcium hydride in spot.
6413·54	6				2	

TABLE V.—Enhanced Lines of Scandium.

Compared with Sun, Spots, and Chromosphere.

Scandium (FOWLER).		Sun (ROWLAND).		Sun-spots.		Chromosphere (DYSON).		Remarks.
				HALE.	FOWLER.			
Wave-length.	Intensity.	Wave-length.	Intensity.	Intensity.	Intensity.	Wave-length.	Intensity.	
4014·65	2	(Fe 14·68)	5		n.c.	Sc, Fe, 14·77	1	Compound line in Sun.
4247·00	10	Sc 47·00	5	6	n.c.*	Sc 47·00	10	* n.c. indicates "no change."
4294·94	4	Zr 94·94	2		n.c.	– 95·2	1	
4305·88	4	– 05·87	2		n.c.	Sr, Ti 05·83	3	Compound line in chromosphere.
4314·25	7	Sc 14·25	3	3–4	n.c.	Sc 14·31	2	
4320·91	7	Sc 20·91	3		n.c.	Sc, Ti 20·98	4	Compound line in chromosphere.
4325·15	6	Sc 25·15	4		n.c.	Sc 25·25	1	
4354·78	4	– 54·78	1		n.c.	– 54·61	1	
4374·68	8	Sc, Fe ? 74·63	3		n.c.	(Y 75·14)	7*	* Includes Sc 74·68, pTi 74·90, and pY 75·10 (LOCKYER).
4384·97	3	– 84·99	0		*			*Masked by strengthened V 84·87.
4400·56	8	Sc 00·56	3	3–4	n.c.	Sc 00·67	3	
4415·72	7	– 15·72	3	2–3	n.c.	Sc 15·65	2	
4420·83	1	– 20·83	00		oblitd.			
4431·53	1	– 31·53	0	0–1	*			* Strengthening probably due to Ti 31·46.
4670·59	6	– 70·59	2		? *	Sc 70·45	2	* Somewhat strengthened on red edge, probably due to line of another element.
						YOUNG.		
						Wave-length.	Fr. Br.*	* "Frequency" and "brightness."
5031·20	6	– 31·20	3		1–2	5031·3	4 3	
5239·99	5	– 39·99	1		00	5240·0 *	3 2	* High-level line (FOWLER).
5318·52	2	– 18·53	00		oblitd.			
5527·03	10	– 27·03	3		2	5527·0 *	40 5	* High-level line. YOUNG'S line 5525·9 (A°) identified with this by MITCHELL and FOWLER, wrongly corrected to 5528·64 in SCHEINER.
5641·21	4	– 41·21	1		0	5641·66*	1 1	* Probably wrongly corrected from 5640·2 (A°).
5658·10	7	– Y 58·10*	2	1–2	1–2	5658·10	8 3	* Y not given by THALÉN or KAYSER.
5658·56	2	– 58·56	0		000			
5667·40	3	– 67·37	0		00	5667·7 *	1 1	* Probably wrongly corrected from 5666·0 (A°).
5669·28	4	– 69·26	1	0	0	5669·2	2 2	
5684·43	5	– 84·42	1		0	5684·7 *	5 3	* This is a line of Si in Sun, but λ may have been wrongly corrected from 5683·5 (A°) or may be mistaken identification with solar line.
6245·85	4	– 45·83	1		00			
6279·95	4	– 79·95	0		*			* Probably weakened, but difficult on account of air line 80·11.
6300·85	1	– 00·90	000		1*			* Spot line probably not Sc.
6310·15	2	*						* Confused with air line 10·10 (2).
6321·06	2	– 21·07	00		oblitd.			

XVII. *The Spectrum of Magnesium Hydride.*

By A. Fowler, *A.R.C.S., F.R.A.S., Assistant Professor of Physics, Imperial College of Science and Technology, South Kensington.*

Communicated by Prof. H. L. Callendar, *M.A., LL.D., F.R.S.*

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[Plates 12, 13.]

Introductory.

In a paper communicated to the Royal Astronomical Society in June, 1907, I gave a preliminary account of my identification of a number of hazy "band lines" in the spectra of sun-spots with lines composing the green fluting in the spectrum of magnesium hydride.* Previous observations had suggested that the origin of these lines was most likely to be traced by the examination of fluted spectra, but numerous measurements of the flutings of substances such as vanadium and titanium, the lines of which are specially prominent in the spot spectrum, gave only negative results.† In December, 1906, however, Mr. Newall published an account of some observations of sun-spots in which reference was made to a probable dark fluting beginning at 5210·2 or 5211·0,‡ and this observation recalled the principal fluting of magnesium hydride with which I had long been familiar. No sufficiently precise measurements of the components of the fluting were then available for a satisfactory comparison, but new determinations of wave-lengths, based on a large-scale photograph taken for the purpose, left no doubt as to the identity of the stronger components with the principal band lines of the spots in the region considered. It seemed probable that several hundreds of these band lines would eventually be accounted for by magnesium hydride, and that the problem presented by the highly complex spot spectrum would be greatly simplified if the part due to the flutings could be completely eliminated.

The present paper gives an account of a more complete investigation of the

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* 'Monthly Notices,' vol. 67, p. 530 (1907).

† 'Trans. Internl. Union Solar Research,' vol. 1, p. 217 (1906).

‡ 'Monthly Notices,' vol. 67, p. 170 (1906).

22.10.09

magnesium hydride spectrum, and includes a table of wave-lengths for the three principal flutings, which it is believed will be of service to those who are engaged in the reduction of photographs of the sun-spot spectrum.

Methods of Producing the Spectrum.

The magnesium hydride spectrum appears to have been first observed and investigated by LIVEING and DEWAR in 1878.* In the course of their experiments on the reversal of metallic lines, these observers recorded an absorption "line" near 5210 (corresponding to the first head of the green fluting), and concluded that it must be attributed either to magnesium or to magnesium together with hydrogen. The same "line" was afterwards observed in the spectrum of the spark between magnesium points in an atmosphere of hydrogen,† the line being most constantly visible when no jar was employed. With a small Leyden jar in the circuit, the line was still visible, but it was not seen continuously when a large jar was used until the pressure of the hydrogen, and its resistance, were very much reduced. In these experiments the fluted character of the spectrum was clearly brought out.‡

In another paper§ it was further remarked that the line 5210 and the series of fine lines which accompany it were sometimes seen in the flame of burning magnesium, but appeared with increased brilliance if the burning magnesium were held in a jet of hydrogen, of coal gas, or of steam.

The spectrum has also been investigated to some extent by Sir NORMAN LOCKYER,§ whose observations were chiefly made on magnesium ribbon burning in the interior of a Bunsen flame. This is, perhaps, the readiest method of producing the spectrum for observation with small instruments, but is unsuitable as a source intended for photography with high dispersion.

The most convenient source which I have yet found is the electric arc between magnesium rods in an atmosphere of hydrogen, preferably at from 1 to 3 inches pressure. The spectrum is also well seen if the arc be simply passed in an exhausted globe, as a sufficient supply of hydrogen is liberated from the heated poles after a few minutes' running.‖ In this way the spectrum is obtained sensibly free from impurity lines, and shows little more than the lines of magnesium (and sometimes those of hydrogen) in addition to the flutings of the hydride.

The construction of the apparatus employed for this experiment will be gathered from fig. 1. A glass receiver of 2 or 3 litres capacity was selected, having 2 necks, and a side tube about 6 inches in length, which was closed by a plate of glass or quartz. The lower pole-piece was attached to a narrow brass tube passing through a

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[*] 'Roy. Soc. Proc.,' vol. 27, p. 352 (1878).

[†] 'Roy. Soc. Proc.,' vol. 27, p. 494 (1878).

[‡] 'Roy. Soc. Proc.,' vol. 30, p. 96 (1880).

[§] 'Roy. Soc. Proc.,' vol. 30, p. 27 (1879); vol. 43, p. 122 (1887).

[‖] FOWLER and PAYN, 'Roy. Soc. Proc.,' vol. 72, p. 254 (1903).

rubber stopper which fitted tightly into the lower neck of the flask. The upper pole was attached to a similar brass tube and rubber stopper, but in order to allow of the manipulation of the arc, the stopper was not placed directly into the upper neck of the flask, but was connected with it by a wide rubber tube about 4 inches in length, kept stretched by a spiral spring inside it. The upper tube was connected with the pump and the lower one with the gas supply, communication with the interior of the globe being made through small apertures drilled in the brass tubes near the pole-pieces. This arrangement was found quite satisfactory so long as the apparatus was not allowed to become overheated, and intermittent exposures extending over several hours could be made before the window through which the arc was viewed became too clouded for further use. The current ordinarily employed was from 2 to 6 amperes, derived from the 110-volt lighting circuit, and showing a potential difference of 40 volts between the poles.

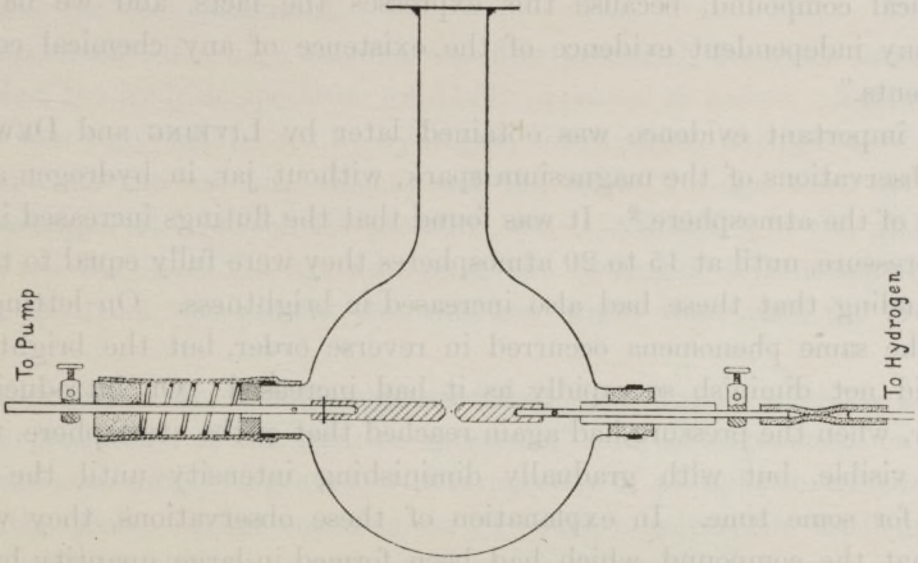

Fig. 1. Apparatus employed for arc *in vacuo*, hydrogen, or other gas.

A convenient method of producing the spectrum has also been described by Mr. Brooks,* who has obtained the flutings very brilliantly from a "high-frequency flame discharge" between magnesium ribbon spirals in hydrogen at low pressures. In a later paper† Mr. Brooks refers to other experiments on the mode of production of this spectrum.

Considerations as to the Origin of the Flutings.

The outcome of the numerous experiments made by Liveing and Dewar was to indicate that hydrogen, in some form or other, was as necessary as magnesium for the production of the spectrum under consideration. Summarising their earlier results in

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* 'Roy. Soc. Proc.,' A, vol. 80, p. 218 (1908).

† 'Astrophys. Jour.,' vol. 29, p. 177 (1909).

1880, these observers stated that "if it (the line 5210 at the head of the green fluting) be not due to a compound of magnesium with hydrogen, at any rate it occurs with special facility in the presence of hydrogen, and ought to occur in the sun if the temperature were not too high. We have been careful to ascribe this line and its attendant series to a mixture of magnesium and hydrogen rather than to a chemical compound, because this expresses the facts, and we have not yet obtained any independent evidence of the existence of any chemical compound of these elements."

Further important evidence was obtained later by LIVEING and DEWAR from a series of observations of the magnesium spark, without jar, in hydrogen at pressures above that of the atmosphere.* It was found that the flutings increased in brilliancy with the pressure, until at 15 to 20 atmospheres they were fully equal to the *b* group, notwithstanding that these had also increased in brightness. On letting down the pressure, the same phenomena occurred in reverse order, but the brightness of the flutings did not diminish so rapidly as it had increased. On introducing a large Leyden jar, when the pressure had again reached that of the atmosphere, the flutings were still visible, but with gradually diminishing intensity until the spark had continued for some time. In explanation of these observations, they wrote: "It appears that the compound, which had been formed in large quantity by the spark without jar at the higher pressures, is only gradually decomposed, and not re-formed by the high temperature of the spark with jar. This experiment, which was several times repeated, is conclusive against the supposition that the flutings are merely due to a lower temperature." Hence it was concluded that "the series of lines beginning at wave-length 5210 are due to a combination of hydrogen with magnesium, and are not dependent solely upon the temperature."

Since then the spectrum in question has been generally known as that of "magnesium hydride," and as no sufficient reason has appeared for assigning a different origin, this designation has been retained in the present paper.

I have at various times repeated many of the experiments described by LIVEING and DEWAR (but not yet including the spark under pressure), and have obtained results in complete accordance with those to which they referred. Additional observations made during the present investigation may also be mentioned. For example, when the arc was passed between magnesium poles in a nearly exhausted globe, no trace whatever of the hydride flutings was seen on first starting the arc, but the oxide group beginning at 5007 was a conspicuous feature of the spectrum. After 2 or 3 minutes' running, however, the oxide group entirely disappeared, while the hydride flutings gradually made their appearance and finally became very brilliant. These observations are most simply explained by supposing that the residual oxygen present in the globe at the beginning of the experiment was gradually consumed, forming magnesium oxide, while hydrogen was liberated when the poles became heated and entered into combination with the magnesium vapour in the outer parts of the arc. Other experiments have shown that hydrogen is occluded in considerable quantity in the metal, and, in fact, the C and F lines were often present in the spectrum, although no hydrogen was otherwise introduced into the globe. Attempts to completely expel the occluded hydrogen from the metal employed have not been successful.

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* 'Roy. Soc. Proc.,' vol. 32, p. 198 (1881).

In this experiment, if a high vacuum was first produced, the oxide bands were not seen at all, but the hydride spectrum gradually appeared as before. Again, when the residual air was first washed out by hydrogen, the hydride flutings were brilliantly visible as soon as the arc was struck, and the oxide flutings were not observed. When dry nitrogen at atmospheric pressure was introduced into the globe, neither the hydride nor the oxide flutings were seen. In hydrogen at atmospheric pressure the hydride spectrum was present, but was less bright than when the pressure was reduced.

In his earlier paper, Mr. BROOKS suggested that water vapour might be an essential factor in the production of the hydride spectrum,* and the experiment on the arc in hydrogen was accordingly repeated, with a quantity of phosphoric anhydride introduced into the globe. After standing for 24 hours, however, the flutings appeared at once on striking the arc, as in previous experiments, and with undiminished brightness. In fact, the absence of water vapour would seem to be sufficiently indicated by the absence of the oxide group 5007. Subsequent experiments made by Mr. BROOKS† have similarly led him to conclude that the presence of water vapour cannot be regarded as an essential condition for the production of the hydride spectrum.

All the experiments accordingly tend to show that magnesium and hydrogen are together concerned in the production of the flutings, and the simplest supposition is that they originate in the combination magnesium hydride. Assuming such combination of the two elements, it appears to take place directly under the influence of the arc, especially at low pressures, or of some forms of the spark discharge, or by the combustion of the metal in an atmosphere containing hydrogen either free or in combination.

It should be noted that the production of the hydride flutings is not the only effect of hydrogen on the magnesium arc spectrum. The enhanced lines also appear very prominently,‡ but they are especially developed close to the poles, while the flutings are not so restricted. Since these lines may be obtained in other ways, unaccompanied by the flutings, without the aid of hydrogen (as in the ordinary spark in air), it is probable that no chemical action is involved in their production in the arc in hydrogen. On the other hand, the flutings in question have only been produced in the presence of hydrogen, and since they may be obtained without direct electrical aid (as in burning the metal in a Bunsen flame), a chemical union of the two elements provides the most satisfactory explanation of the observations.

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* 'Roy. Soc. Proc.,' A, vol. 80, p. 223 (1908).

† 'Astrophys. Jour.,' vol. 29, p. 187 (1909).

‡ The enhanced lines which appear in the visible spectrum are 4481·31, and the pairs of lines for which the revised wave-lengths are 4434·20, 4428·20 and 4390·80, 4384·86. The polar localisation of these lines as compared with the flutings is particularly marked in a photograph taken with one pole of magnesium and one of iron. In another photograph, where the images of the poles appear to have been successfully kept off the slit, 4481 was relatively weak, and the feebler enhanced lines were wanting.

One of the chief objections to the above explanation of the flutings is that, although the spectrum may be easily produced, the compound itself has not yet been clearly recognised by chemists. WINKLER* possibly obtained it as part of a mixture resulting from heating magnesium with its oxide in an atmosphere of hydrogen, but no other chemical evidence of the existence of the compound has been brought forward. Further evidence has been sought by an analysis of the deposit formed by the passage of the arc in hydrogen. This consisted in part of thin spherical shells of magnesium, and partly of a fine black or dark grey powder, probably mixed, as a rule, with a small proportion of magnesium oxide. The analysis of this deposit was kindly undertaken by Prof. TILDEN, who reports that the volume of hydrogen given off on dissolving the sample supplied was always less than the amount calculated on the supposition that it was pure magnesium, and that there was no evidence of a hydride. This was, perhaps, only to be expected from the observation that there was no appreciable absorption of hydrogen during the passage of the arc, but there was the possibility that such absorption might be partly counteracted by the liberation of hydrogen from the heated poles.

In explanation of the spectroscopic observations, on the hypothesis that the flutings are produced by magnesium hydride, it may be supposed that a very small quantity of the compound is competent to produce a brilliant spectrum. The compound would not be unique in this respect, as the cyanogen flutings are ordinarily well developed in experiments on carbon compounds even if only a very small trace of nitrogen be present. Or it may be, as suggested by Mr. BROOKS, that the compound is in most experiments decomposed as quickly as it is formed. A perfectly definite conclusion does not at present seem to be possible.

The Spectrographs Employed.

For obtaining a general record of the visible spectrum, a small Littrow prismatic spectrograph, giving the region C to K on a plate 6½ inches long, was employed. The photograph reproduced in Plate 12, No. 1, was taken with this instrument.

Numerous photographs were also obtained with a larger instrument of the same type, giving the region 6700 to 4700 on a 12-inch plate. A great deal of time was spent in reducing these photographs, using ROWLAND'S wave-lengths, but a concave grating of greater resolving power afterwards became available and the results were discarded.

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* 'Ber. Deutsch. Chem. Gesell.,' vol. 24, p. 1973 (1891).

The concave grating was ruled by ROWLAND, and has a radius of curvature of 10 feet, and a ruled space $3\frac{1}{4}$ inches by $1\frac{5}{8}$ inches. It was mounted temporarily as a Littrow spectrograph by Mr. EAGLE, and the photographs were taken on plates 12 inches by $2\frac{1}{2}$ inches. In the first order, the dispersion is about $5\frac{1}{2}$ tenth-metres to the millimetre, but in this method of using the grating the spectrum is not a normal one. Excellent photographs of the first-order spectrum were obtained with exposures ranging from 5 to 90 minutes, and the definition was very satisfactory. Photographs have also been taken in the second order, showing the principal lines of the green and blue flutings, but giving no impression of the fainter fluting in the yellow green.

A general record of the ultra-violet spectrum, extending to 2300, has been obtained by the use of a Hilger quartz spectrograph having one prism of 60 degrees.

General Description of the Spectrum.

When observed with small or moderate dispersion (Plate 12A, No. 1), the spectrum of magnesium hydride, as remarked by LIVEING and DEWAR, is somewhat similar in general appearance to the carbon ("Swan," or candle flame) spectrum, and the respective flutings occupy nearly the same parts of the spectrum. In each case the brightest fluting is in the green, and there are fainter ones in the yellow-green and blue, the first heads of the carbon flutings being at 5635·4, 5165·3, and 4737·2, while those of magnesium hydride fall at 5621·6, 5211·1, and 4844·9. Further, there is a fluting of simple structure at 4311 in the hydrocarbon spectrum, and a somewhat similar fluting of magnesium hydride at 4371·8.

On more minute examination, however, the resemblance is less close than might at first appear. Even under moderate dispersion the blue flutings in the two spectra are clearly of different structure, and they have practically nothing in common when the dispersion is great. The green and yellow-green flutings in the two spectra resemble each other in showing three or four heads, but whereas in the case of carbon the secondary heads persist under high dispersion, those of magnesium hydride are soon lost in the general mass of lines as the dispersion is increased.

From the extreme visible red to the beginning of the yellow-green fluting at 5621 the spectrum consists of a great number of faint lines, showing no heads sufficiently pronounced for measurement as such, though the lines are by no means equally spaced. (The carbon arc shows a very similar appearance in this region.) The yellow-green fluting begins with a series of rather faint lines, but stronger lines appear in the more refrangible part, and the components can be traced to the head of the next group. The green fluting beginning at 5211 also has its strongest lines a considerable distance from the first head, and becomes very faint as it approaches the blue band. Still greater complexity is shown by the blue group of flutings, which has its greatest intensity in the region about 4780, and can be followed to the violet head at 4371. The spectrum, in fact, shows an almost unbroken succession of lines at very short intervals throughout the entire visible spectrum, but the lines are mostly faint, except in the definite flutings to which reference has been made.

The ultra-violet spectrum, of which no measurements have yet been undertaken, also exhibits a great number of lines distributed throughout its whole extent. There is a well-marked fluting, very similar to the one in the green, with its head about 2430, and fading off on the more refrangible side. There is also an interesting series of double lines in the region about 2940 to 3100, in which the lines close up towards the side of shorter wave-length, whereas the somewhat similar series which can be traced in the green and yellow-green flutings converge towards the red.

Another feature of the spectrum, which cannot be very clearly seen in the reproductions, is possibly of some importance. On photographs which have received sufficient exposure, there are patches of unresolved continuous background, sometimes terminated by strong lines, but often by lines which are very faint and indistinct. Intervening places in the spectrum, varying in width from about 0·3 tenth-metre upwards, remain conspicuously clear in the negatives, and have the appearance of bright lines or narrow bright bands.

Similar patches of "dark ground" have been noted by KAYSER and RUNGE in their account of the 3883 fluting of cyanogen,[*] and the same appearance may be seen in the flutings of titanium oxide and other substances. This appearance, however, does not seem to be special to fluted spectra, as regions of dark ground and exceptionally clear spaces are also found in negatives of the crowded ultra-violet arc spectrum of iron. In the latter case, the darker places are probably due to groups of closely adjacent faint lines, or to an underlying banded spectrum, and the darker places in fluted spectra may similarly be due to groups of faint lines. Attempts to indicate the positions of the dark and bright places in the magnesium hydride spectrum were abandoned, on account of the difficulty of dealing with differences depending upon the dispersion employed and upon differences of exposure.

Determination of Wave-lengths.

The catalogue of wave-lengths which appears at the end of the present paper has been based entirely upon photographs with iron arc comparisons, taken with the concave grating of 10 feet radius. The new standard wave-lengths determined by FABRY and BUISSON[†] were adopted for the iron lines, and as many as possible of these lines were included in each section of the spectrum measured, so as to furnish a check on the general accuracy of the work. In order to eliminate local systematic errors as far as possible, each of the three flutings to which the catalogue refers was at least once completely measured with the same setting of the plate.

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[*] 'Abh. K. Preuss. Akad. Wiss.,' Berlin, 1889.

[†] 'Astrophys. Jour.,' vol. 28, p. 195 (1908).

As the spectra were not normal, interpolations were made by equations of the form

$$\lambda = a+bs+cs^2,$$

where λ and s refer to corresponding wave-lengths and micrometer-scale readings, and a, b, c are constants calculated from three of the standard lines. All the standard lines might be made to contribute to the adopted values of a, b, c by the laborious method of least squares, but the gain was found to be scarcely appreciable in a case to which it was applied.

The following example, taken from the measurements of a second-order photograph of the green fluting, will show the accuracy with which the dispersion of the grating over a moderate range may be represented by the above equation. It will also indicate the increased precision which is made possible by the new interference wave-lengths for the iron arc lines as compared with the use of ROWLAND'S values for the absorption lines of iron which occur in the Fraunhofer spectrum.

Equation for FABRY and BUISSON scale :—

$$\lambda = 5260{\cdot}520 - 2{\cdot}67595s + 0{\cdot}000136s^2.$$

Equation for ROWLAND'S scale :—

$$\lambda = 5260{\cdot}678 - 2{\cdot}67544s + 0{\cdot}000132s^2.$$

s in mm.	λ (F. and B.).	O – C.	λ (R).	O – C.	
10·305	5232·958*	000	5233·122*	000	* Used in calculation of constants.
25·502	5192·362	– 004	5192·523	– 012	
34·827	5167·492	+ 002	5167·678	+ 017	
56·257	5110·415	+ 005	5110·574	– 010	
66·435	5083·343*	000	5083·518*	000	
79·055	5049·827	+ 004	5050·008	+ 012	
93·287	5012·072	– 001	5012·252	+ 009	
97·132	5001·880	– 003	5002·044	– 008	
110·645	4966·104*	000	4966·270*	000	

An alternative method of reduction was employed in duplicating the work for the detection of numerical errors. In this case, the two extreme iron lines in each section of the spectrum were employed as standards for the calculation of linear equations, and from the values of O – C for the intermediate standards, curves of error were drawn, from which the corrections to normal were readily derived. Numerous additional checks were also made by simple linear interpolations between iron standards not more than 40 tenth-metres apart.

In spite of every precaution, some of the grating photographs showed small displacements of the magnesium spectrum with reference to the iron comparison, probably arising from the effects of varying temperature during the longer exposures.

The magnitudes of these displacements were determined by reference to the ordinary lines of magnesium, and partly by comparison with wave-lengths derived from photographs of magnesium hydride taken with one pole of iron, and presumably showing no relative displacement.

The stronger lines of the green fluting were measured on second-order photographs, and where the results from different plates were in sufficient accordance, the wave-lengths in the catalogue have been stated to seven figures. It is not claimed, however, that the third decimal is entitled to any great weight, but it has in some cases been found desirable to retain it in the discussion of series lines.

The lines composing the blue group are, on the whole, much fainter than those of the one in the green, so that, although the stronger lines were measured on second-order plates, the accuracy is probably less than that for the green fluting, and the resulting wave-lengths are stated to six figures only. The fainter lines of the blue and green flutings, and the whole of the yellow-green, were determined from photographs of the first-order spectrum, but it is hoped that the errors will rarely exceed 0·02 or 0·03 tenth-metre, except possibly in the case of doubles which are barely resolved.

Retention of Rowland's *Scale.*

As the immediate use of the magnesium hydride wave-lengths is for comparison with the sun-spot spectrum, it has been thought desirable to convert them from the scale of Fabry and Buisson, on which they were computed, to that of Rowland. A very complete investigation of the relation between the two scales has been made by Hartmann,[*] who has advocated the general adoption of a slightly modified Rowland scale, which would have the advantage of demanding only small changes in the existing tables of wave-lengths. After due consideration, however, it has been thought that immediate needs would be best met by expressing the magnesium hydride wave-lengths as nearly as possible on the Rowland scale now in use; that is, the scale of the "Preliminary Table of Solar Spectrum Wave-lengths." Comparison of Rowland's solar wave-lengths with the new standards shows that this may be accomplished by adding 0·170 tenth-metre to the values on the Fabry and Buisson scale from 4370 to 5365, and 0·218 tenth-metre from 5365 to the head of the yellow-green band at 5621. The tabulated wave-lengths (in the catalogue at the end of this paper) have accordingly been expressed on this system, and may, therefore, be directly compared with Rowland's solar wave-lengths without introducing errors of inconvenient magnitude. At the same time the wave-lengths stated in this way retain some of the advantages resulting from the use of the new standards, and are directly available for investigations of the series relationships of the different lines, provided that 0·05 be subtracted from the tabulated wave-lengths on the less refrangible side of 5365 when connecting lines on the two sides of this position.

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[*] 'Astrophys. Jour.,' vol. 18, p. 167 (1903); 'Physikalische Zeitschrift,' 10. Jahrg., No. 4, p. 121 (1909).

Moreover, the wave-lengths may readily be reconverted to the Fabry and Buisson scale if so desired.

The Intensity Scale.

The intensities of the various lines have been roughly estimated on a scale of 10 for the strongest lines, ranging down to 1 for the fainter of the well-marked lines. For the faintest lines 0, 00, and 000 have been employed, in accordance with the convenient system adopted by ROWLAND; these are only visible on the plates which have received comparatively long exposures, and 000 is at the limit of visibility. Many of the lines are probably composite, so that a line of stated intensity may sometimes be made up of two or more lines of lower intensity.

Series Lines in the Green Fluting.

A preliminary analysis of the wave-lengths has been made for the purpose of establishing series relationships between the lines of magnesium hydride, and thus obtaining a general check on the accuracy of the wave-length determinations. Some of the related lines were readily picked out by inspection, especially those proceeding from the first heads of the green and yellow-green flutings. Others were identified by their occurrence in pairs, and by the approximate constancy of the second differences between the wave-lengths of successive lines of the series.

The more striking of the probable series occurring in the green fluting are indicated in the general wave-length table by the use of the letters α, β, &c., to mark the associated lines. They are also shown graphically in Plate 12B. The yellow-green fluting exhibits similar series, but the "stride" is considerably larger than in the series composing the fluting in the green. The blue group of flutings is extremely complicated, and no attempt has yet been made to resolve it into its component series.

Many lines which were measured and tabulated as single lines appear to belong to two or more of the series, and it is, therefore, probable that such lines are very close doublets or triplets which could not be separated with the resolving power of the instrument employed. The same conclusion is also indicated by the greater intensities of these lines as compared with adjacent members of the component series. On account of this composite character of many of the lines, and partly for the lack of an exact formula to connect the lines belonging to a given series, the series inquiry does not furnish a complete test of the accuracy of the measurements. Nevertheless, there is sufficient evidence to indicate that the values tabulated cannot be greatly in error.

The general structure of a series will be gathered from the following table, showing the first and second differences between the wave-lengths of the lines composing the α series:—

λ.	First differences.	Second differences.	
5211·115			
	0·226		
10·889		258	
	0·484		
10·405†		166	
	0·650		
09·755		240	
	0·890		
08·865		214	
	1·104		
07·761		215	
	1·319		
06·442		218	
	1·537		
04·905		209	† Probably a compound line.
	1·746		
03·159		221	
	1·967		
5201·192		216	
	2·183		
5199·009		198	
	2·381		
96·628		209	
	2·590		
94·038		202	
	2·792		
91·246		226	
	3·018		
88·228		216	
	3·234		
5184·994			

It will be seen that, apart from the influence of a probably compound line, the second differences are sensibly constant throughout the range of visibility of this short series. In the case of the longer series the second differences diminish in passing from the heads, and they are apt to be less regular in the more refrangible parts of the flutings because of the greater overlapping of different systems and the consequent uncertainty as to the wave-lengths of the components of the unresolved lines.

Some of the formulæ which have been suggested for the mathematical representation of series have been tested on series identified in the green fluting. In place of the oscillation frequencies which should strictly have been employed, all the calculations have been made in terms of wave-lengths. In short series the possible error introduced in this way is inappreciable, and some of the equations used are of the same form whether frequencies or wave-lengths are used.

DESLANDRES' simple formula

$$\lambda_m = a - bm^2,$$

where λ is the wave-length, a and b are constants, and m has integer values, is quite inadequate for the magnesium hydride series.

The modification employed by HIGGS,* or its equivalent

$$\lambda_m = a - b\,(m+\mu)^2,$$

where μ is an additional constant, usually gives only small errors when applied to about a dozen lines, and may, therefore, be employed for the shorter series. By expanding this equation, it assumes the form used by LESTER† for the oxygen bands of the solar spectrum, namely,

$$\lambda_m = a - bm - cm^2.$$

This is somewhat more convenient for purposes of calculation, and the following examples will indicate the accuracy with which it represents the four short series proceeding from the head of the green fluting. The magnitudes of O–C (observed *minus* computed values) are expressed in thousandths of a tenth-metre.

$$\begin{aligned}
&\alpha \text{ series}: &\lambda_m &= 5211{\cdot}115 - 0{\cdot}141m \;- 0{\cdot}1067m^2,\\
&\beta \quad ,, &\lambda_m &= 5210{\cdot}405 - 0{\cdot}3673m - 0{\cdot}10603m^2,\\
&\gamma \quad ,, &\lambda_m &= 5210{\cdot}582 - 0{\cdot}5435m - 0{\cdot}10094m^2,\\
&\delta \quad ,, &\lambda_m &= 5209{\cdot}940 - 0{\cdot}4891m - 0{\cdot}11317m^2.
\end{aligned}$$

m.	O – C.			
	α.	β.	γ.	δ.
0	0*	0*†	0*	0*†
1	+22	+ 8†	+ 2†	+14
2	− 1†	+34	−18	−14
3	+23	+33	+ 2	−10
4	+21	+33	0*	− 8
5	+18	+28	−13	0*
6	+14	+20	−20	− 9
7	+ 5	0*	− 8	− 1
8	+ 1*	+ 6	0*	+11
9	−11	− 1	+57	0*
10	−26	+ 1	+155	
11	−25	+13		
12	−20	+ 7		
13	− 4	+19		
14	0	− 1*		
15	+ 1*			

* Employed in determinations of constants in equations.

† Probably compound lines.

Apart from the probably composite lines, the differences between the observed wave-lengths and those calculated from the formulæ, although small, are largely systematic and are apparently due chiefly to the impossibility of accurately representing the series by equations of so simple a type. The equation is especially unsuited to the γ series, assuming that the last lines have been correctly assigned; the second differences in this case vary rapidly towards the end, and only the first nine lines are reasonably represented by the equation.

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* 'Roy. Soc. Proc.,' vol. 54, p. 200 (1893).

† 'Astrophys. Jour.,' vol. 20, p. 81 (1904).

The long series marked ϵ and ζ, which comprise many of the stronger lines of the green fluting, provide a better test of formulæ which have been proposed, and it may be of interest to refer to some of the results obtained for the ϵ series, which includes about forty lines extending over a region of about 160 tenth-metres.

When calculated for the first thirteen lines of the ϵ series, LESTER's equation gives no error as great as 0·01 tenth-metre, but if eight additional lines are included, and the two extreme lines are used in the calculation of constants, the maximum errors exceed 0·1 tenth-metre, and the formula is clearly inapplicable to the whole series. Better results have been obtained by including another term in the equation, but an appreciable systematic error remains even if only lines between the first and twenty-second are employed in the determination of constants. If applied to the whole series, this extended form of LESTER's equation gives systematic errors which reach a maximum of 0·15 tenth-metre.

Another equation which has been tested on the ϵ series is that deduced by HALM* from one adapted to line series, namely,

$$\frac{1}{\lambda_0-\lambda_m} = \frac{\alpha}{(m+\mu)^2}+\beta,$$

where the constants λ_0, α, β and μ are calculated from four of the lines. This represents the first twenty-one lines with an accuracy nearly equal to that of the measurements, but considerable systematic errors remain when it is applied to the whole series. The true equation connecting the lines of a fluting series, therefore, remains to be discovered, and until some progress has been made in this direction, and still greater dispersion can be effectively employed, it does not seem worth while to pursue the matter further.

The numerical results of the calculations for the ϵ series, however, may be useful to those interested in this inquiry, and they are accordingly brought together in the appended table. Numbers below the horizontal lines are results of extrapolation.

Comparison with the Sun-spot Spectrum.

It is interesting to recall that the possible local occurrence of magnesium hydride in the sun was clearly recognised by LIVEING and DEWAR in their paper of 1880.† Referring to the head of the green fluting at 5210, they wrote: "A line of the same wave-length has been seen by YOUNG in the chromosphere once. Its absence from the Fraunhofer lines leads to the inference that the temperature of the sun is too high

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[*] 'Trans. Roy. Soc. Edin.,' vol. 41, p. 551 (1905).

[†] 'Roy. Soc. Proc.,' vol. 30, p. 97 (1880).

CALCULATIONS of ϵ Series.

LESTER'S formula

$$\lambda_m = 5183 \cdot 364 - 1 \cdot 118m \;- 0 \cdot 08879m^2 \quad . \;.\;.\;.\;.\;.\;. \quad (1)$$

$$\lambda_m = 5183 \cdot 364 - 1 \cdot 14475m - 0 \cdot 08617m^2 \quad . \;.\;.\;.\;.\;.\;. \quad (2)$$

$$\lambda_m = 5183 \cdot 364 - 1 \cdot 0941m \;- 0 \cdot 094296m^2 \;+ 0 \cdot 0002808m^3 \quad . \;.\;. \quad (3)$$

$$\lambda_m = 5183 \cdot 364 - 1 \cdot 03835m - 0 \cdot 1011146m^2 + 0 \cdot 00047434m^3 \quad . \;.\;. \quad (4).$$

HALM'S formula

$$\frac{1}{5186 \cdot 642 - \lambda_m} = \frac{10 \cdot 7384}{(m+5 \cdot 938)^2} + 0 \cdot 00053 \quad . \;.\;.\;.\;.\;.\;.\;. \quad (5)$$

$$\frac{1}{5186 \cdot 428 - \lambda_m} = \frac{10 \cdot 45245}{(m+5 \cdot 665)^2} + 0 \cdot 0006743 \quad . \;.\;.\;.\;.\;.\;.\;. \quad (6).$$

λ.	m.	O – C (in thousandths of 1 tenth-metre).					
		1.	2.	3.	4.	5.	6.
5183·364	0	0*	0*	0*	0*	0*	0*
82·149	1	– 8	+ 16	– 27	– 76	– 21	– 41
80·764	2	– 9	+ 34	– 37	– 123	– 28	– 64
79·207	3	– 4	+ 53	– 34	– 145	– 25	– 72
77·476	4	+ 4	+ 69	– 21	– 147	– 13	– 69
75·556	5	+ 2	+ 70	– 15	– 148	– 10	– 69
73·460	6	0*	+ 66	– 4	– 136	– 3	– 63
71·181†	7	– 6	+ 53	0*	– 123	0*	– 58
68·734	8	– 4	+ 43	+ 14	– 95	+ 11	– 41
66·104	9	– 6	+ 22	+ 21	– 70	+ 16	– 30
63·300	10	– 5	0*	+ 26	– 43	+ 20	– 17
60·324	11	+ 3	– 21	+ 31	– 15	+ 26	– 2
57·163	12	+ 1*	– 55	+ 21	0*	+ 17	0*
53·826	13	+ 2	– 94	+ 4	+ 7	+ 2	– 4
50·335†§	14	+ 26	– 113	0*	+ 25	0*	+ 4
46·689	15	+ 73	– 116	+ 6	+ 50	+ 8	+ 21
42·868	16	+ 122	– 121	– 1	+ 60	+ 4	+ 26
38·885†	17		– 115	– 7	+ 65	0	+ 27
34·755†	18		– 84	– 1	+ 76	+ 7	+ 38
30·436†	19		– 71	– 25	+ 49	– 17	+ 13
26·003	20		+ 2*	– 8	+ 57	– 1	+ 24
21·404	21		+ 81	0*	+ 44	+ 1*	+ 17
16·636†	22		+ 163	– 9	+ 4	– 17	- 15
11·793	23			+ 60	+ 29	+ 38	+ 19
06·759	24			+ 86	0*	+ 47	0*
5101·590†	25			+ 126	– 30	+ 62	– 20
5096·335	26				– 16		+ 6
90·907	27				– 46		– 14
85·365	28				– 65		– 23
79·700	29				– 83		– 34
73·940	30				– 78		– 23
68·066	31				– 69		– 13
62·060	32				– 79		– 24
56·000	33				– 31		+ 18
49·810†	34				– 5		+ 33
43·500	35				+ 6		+ 28
37·070	36				0*		0*
30·61	37				+ 64		+ 31
5024·03	38				+ 104		+ 33

* Lines used in calculation of constants.

† Probably compound lines, belonging to more than one series.

§ Adopted as ϵ component of compound line for purposes of calculation, in place of wave-length in general table.

(*unless at special times and places*)* for its production. If it be not due to a compound of magnesium with hydrogen, at any rate it occurs with special facility in the presence of hydrogen, and ought to occur in the sun if the temperature were not too high."

There is no evidence of the presence of the fluting as a whole in the chromospheric spectrum, and as the first head line at 5211·11 does not agree accurately with either of YOUNG's lines near its position, it must be concluded that magnesium hydride does not appreciably contribute to the spectrum of the chromosphere. In the sun-spot spectrum, however, the green fluting of magnesium hydride is strongly marked, and at least the stronger components of the yellow-green and blue flutings are also easily traced in the Mount Wilson and Kodaikanal photographs. In the spot spectrum the lines are somewhat hazy, and belong to the class called "band lines" or "umbra lines"; in the regions where they occur they appear to be the more conspicuous of the multitude of lines into which the dark background of the spot spectrum is resolved when high dispersion is employed.†

Complete series of measurements of the band lines of the spot spectrum are not yet available. A few of them have been noted from visual observations by MAUNDER, MITCHELL, and myself, and 127 were tabulated between 5212 and 5032 by HALE and ADAMS from the earlier photographs of the spot spectrum‡ taken at Mount Wilson. Even the latter catalogue, however, is far from complete, although it contributed largely to the first identification of magnesium hydride in the spot spectrum. Under these circumstances, an exhaustive comparison of the two spectra cannot yet be given, and indeed such a comparison is more appropriate to a detailed discussion of the sun-spot spectrum than to the present paper.

A convincing demonstration of the presence of magnesium hydride in spots, however, is afforded by the photographs reproduced in Plate 13, showing the spectra in the region 5212–5062. The photographs of the sun and sun-spot spectra were taken by Mr. EVERSHED at the Solar Observatory, Kodaikanal, India, and were kindly placed at my disposal by the Director, Mr. C. MICHIE SMITH; the exposure given to the sun-spot was about six times as long as that for the sun. The magnesium hydride photograph was taken in the second order of the 10-feet concave grating, and is presented as a negative in order to represent an absorption spectrum. It will be seen that, apart from the interference caused by metallic lines, all the details of magnesium hydride are reproduced in the spot spectrum.§

Effective comparisons of the spot with the yellow-green and blue flutings cannot yet be given, but there is sufficient evidence that many of the band lines in these regions are certainly due to magnesium hydride.

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* The italics are mine.—A. F.

† YOUNG, 'Amer. Jour. of Sci.,' 3rd series, vol. 26, p. 333 (1883). A useful summary of subsequent observations is given by HALE and ADAMS in 'Astrophys. Jour.,' vol. 23, p. 30 (1906).

‡ 'Astrophys. Jour.,' vol. 23, p. 36 (1906).

§ Lines at 5169·96 and 5169·42 in the photograph of magnesium hydride, which do not appear in the spot spectrum, are "ghosts" of b_1 and b_2. Certain other lines in this photograph, as 5197·57 and 5187·26, are relatively too strong in consequence of ghosts which are nearly coincident with them.

To determine exactly the amount of detail in the spot which is accounted for by magnesium hydride will necessarily involve a comparison of wave-length measurements. In this investigation, identity of numerical values must not in every case be expected, in consequence of the presence of so many other lines in the spot spectrum. Thus, the line 5186·59 is evidently combined in the spot with a titanium line at 5186·50, giving rise to an apparent discordance with the wave-length 5186·53 assigned to the spot line by HALE and ADAMS. Such combinations will likewise produce apparent small displacements of the metallic lines. It should be noted also that the apparent intensification of some of the metallic lines, as for example the faint iron line 5177·41, must be due, in part at least, to superposed lines of magnesium hydride, and similarly that in some cases the weakening of metallic lines may be obscured. Further, some of the magnesium hydride lines appear as mere fringes to comparatively strong metallic lines, and are likely to be overlooked if not specially sought. These are some of the points that must be taken into consideration when a minute comparison with the spot spectrum is undertaken.

There is another feature of the spot spectrum which is to some extent explained by the identification of magnesium hydride, namely, the bright interruptions which occur in the dark background of the spot spectrum. YOUNG observed that these interspaces, some of which are quite narrow and look like bright lines, were of the same order of brightness as the undimmed spectrum outside the spots, and the observation has been repeatedly confirmed by others. The account given by HALE, ADAMS, and GALE,[*] from observations made in the 3rd and 4th orders of a Littrow grating spectroscope of 18 feet focal length, may be usefully quoted: "Although an immense number of fine lines can be seen in the spot spectrum, they nevertheless seem to lie on a continuous dark background, which we have not been able to resolve into lines. This background, however, is interrupted at certain points by lines or breaks, which seem to be nearly as bright as the spectrum of the adjacent photosphere. They do not appear to us like genuine bright lines, and we are unable to offer an adequate explanation of them, unless the dark background is resolvable."

As no wave-lengths were given by the Mount Wilson observers, it is not quite certain that the bright interruptions which they observed are identical with those seen in the Kodaikanal photograph of the spot spectrum shown in Plate 13, where the resolving power is not so great. The latter, however, represents very closely the appearance and positions of the bright spaces as observed with the Evershed solar spectroscope employed in my own observations of spots, which gives a purity of about 25,000 near *b*, and a dispersion of 60° from A to H. The great majority of these, in the region about *b*, are coincident with clear spaces in the absorption of magnesium hydride (see p. 454), except, of course, that the latter are sometimes sub-divided, narrowed, or nearly obliterated in the spot spectrum by superposed metallic lines. In the case of magnesium hydride, the gaps are not well displayed as such in the photograph reproduced in Plate 13, but they form a prominent feature in the photograph of the green fluting on Plate 12A, No. 3, which was given a relatively much longer exposure. Among the many gaps common to the two spectra are 5180·9, 5179·4, 5177·2, and 5176·6. It follows, then, that such bright places in the spot spectrum cannot be bright lines superposed on a truly continuous dark background, but simply represent wave-lengths for which magnesium hydride is most transparent. Further investigation is necessary to determine whether the possibly narrower gaps seen with the most powerful instruments are explained in the same manner.

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[*] 'Astrophys. Jour.,' vol. 24, p. 185 (1906).

It may be remarked that magnesium hydride is not the only probable compound which is represented in the spot spectrum. HALE and ADAMS* have shown that the flutings which I identified in the Third-type stars and have attributed to titanium oxide† are a very prominent feature in the red region, and two additional flutings at 6382 and 6389 have been traced to calcium hydride (or, at least, to calcium in the presence of hydrogen) by OLMSTED at the Mount Wilson laboratory.‡ The discovery of these fluted spectra favours the view that spots are regions of local cooling, which was previously suggested by the behaviour of different classes of metallic lines.§

It is probable also that the combined absorption of the thousands of lines belonging to these spectra, extending as they do from the extreme red to the far ultra-violet, contributes materially to the darkness of sun-spots, and absorption corresponding to the "dark ground" occurring in negatives of these spectra will doubtless aid the process of darkening. It cannot be concluded, however, that the absorption of the substances now known to be present in spots is adequate to account entirely for the darkening, as the spot spectrum is darker than the photospheric spectrum in places where the known band spectra are feeble, as, for example, to the red side of the green fluting of magnesium hydride at 5211, and in the ultra-violet region.

A further contribution to the darkness might be made by the scattering of the photospheric light in its passage through the vapours of the spot, or by reduced emission from the underlying photosphere. These, however, would seem to be inadmissible if the bright interruptions of the spot spectrum be really as bright as the corresponding places in the ordinary photospheric spectrum. In visual observations the interruptions certainly appear to be of the same order of brightness as the adjacent photospheric spectrum, but it is difficult to allow for contrast effects, and I am glad to learn that this point is under investigation by photographic methods at Kodaikanal.

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* 'Astrophys. Jour.,' vol. 25, p. 76 (1907).

† 'Roy. Soc. Proc.,' vol. 73, p. 219 (1904); vol. 79, p. 509 (1907). 'Monthly Notices, R.A.S.,' vol. 69, p. 508.

‡ 'Astrophys. Jour.,' vol. 27, p. 66 (1908).

§ FOWLER, 'Trans. Internl. Union Sol. Res.,' vol. 1, p. 228 (1906); HALE, ADAMS, and GALE, 'Astrophys. Jour.,' vol. 24, p. 185 (1906).

Possible Indications of Magnesium Hydride in the Normal Solar Spectrum.

According to the observations of YOUNG* and DUNÉR,† the "band lines" of the sun-spot spectrum, many of which have now been shown to be due to magnesium hydride, would appear to be present as very faint lines in the normal solar spectrum. The same conclusion was also suggested by my own observations,‡ which showed that bright interspaces in the spot spectrum sometimes occupied spaces between nebulous lines of low intensity tabulated by ROWLAND, the lines themselves not being seen with the dispersion available.

From observations made with the very powerful instruments at Princeton, however, W. M. MITCHELL was led to express doubts as to whether the greater part of the band lines are ordinarily exceedingly faint lines in the photospheric spectrum which are brought into prominence by the vapours in the spot, and was inclined to the opinion that the band lines are not present in the photospheric spectrum at all.§ In opposition to this, HALE and ADAMS|| found, from measurements of their large-scale photographs of the spot spectrum, that the wave-lengths of the band lines agreed very closely with the wave-lengths of very faint lines in ROWLAND's tables, and they regarded this as a proof that the substance producing the band lines contributes feebly to the ordinary solar spectrum.

Nevertheless, a critical examination of the table given by HALE and ADAMS, taking account of our present knowledge of the magnesium hydride spectrum, suggests that many of the supposed coincidences are purely accidental. The strongest lines of magnesium hydride, if present at all in the Fraunhofer spectrum, are only represented by lines of intensity 000 or 0000 in ROWLAND's tables, and it is accordingly very improbable that the fainter lines would reveal their presence in any photographs of the solar spectrum now available. Yet some of these faint magnesium hydride lines appear to be identical with band lines then supposed by HALE and ADAMS to correspond with solar lines.

The chief difficulty in arriving at a satisfactory conclusion on this point arises from the fact that there are so many lines in the magnesium hydride spectrum and in the solar spectrum that numerous chance coincidences might be expected even if there were no real relation between the two. The application of the theory of probabilities is somewhat uncertain, and an attempt has therefore been made to obtain further light on the subject by comparing the relative numbers of coincidences of strong and faint lines of magnesium hydride with the solar lines. To allow for possible errors in the two sets of measurements, and for the fact that ROWLAND's standards have not

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* 'Amer. Jour. of Sci.,' 3rd series, vol. 26, p. 333 (1883).

† 'Recherches sur la Rotation du Soleil' (Upsala, 1891).

‡ 'Monthly Notices,' R.A.S., vol. 65, p. 516 (1905).

§ 'Astrophys. Jour.,' vol. 22, p. 4 (1905).

|| 'Astrophys. Jour.,' vol. 23, p. 34 (1906).

been employed in the case of the laboratory spectrum, lines have been considered coincident when they agreed within 0·033 of a tenth-metre. It will suffice to summarise the results of this comparison, which covers the region 5180·7 to 5090·2.

In this region there are 55 lines of intensity 5 and upwards in the magnesium hydride spectrum; 31 of these, or 56 per cent., agree within the specified limit with solar lines; 19, or about 35 per cent., do not agree within this limit; and 5 are certainly or possibly masked by metallic lines.

In the same region there are also 55 magnesium hydride lines of intensity 0 and less, solar coincidences with which must be regarded as accidental. Of these, 22, or 40 per cent., agree with solar lines within the limit stated; 31, or 56 per cent., do not agree; and 2 are probably confused with metallic lines.

The difference in the representation of the two groups of lines is perhaps sufficient to indicate that the stronger lines of magnesium hydride may be really present as very faint lines in the Fraunhofer spectrum, but the evidence is less convincing than might be desired, especially as some of the strongest magnesium hydride lines do not appear in ROWLAND'S catalogue. There is, however, some doubt as to the completeness of ROWLAND'S record of the very faint lines,* and until this is removed no final conclusion can be reached.

Another attempt to obtain evidence upon this point has been based upon the series lines to which reference has already been made. ROWLAND'S relative wave-lengths might be expected to be sufficiently accurate to show nearly constant second differences for lines corresponding to a given series, if the supposed solar coincidences were really significant, but this test cannot be very effectively applied in consequence of the frequent interruption of the possible series by superposed metallic lines. In the case of the ζ series, however, there are five consecutive lines which are free from this complication, details of which are given in the appended table :—

Magnesium hydride.			Sun.		
λ and intensity.	First differences.	Second differences.	λ and intensity.	First differences.	Second differences.
5170·766 (8)			5170·767 (000)		
	2·438			2·407	
68·328 (8)		·174	68·360 (000Nd?)		·207
	2·612			2·614	
65·716 (8)		·184	65·746 (0000)		·230
	2·796			2·844	
62·920 (8)		·180	62·902 (0000)		·112
	2·976			2·956	
59·944 (8)			59·946 (0000)		

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* JEWELL, 'Trans. Internl. Union Sol. Res.,' vol. 1, pp. 49, 50.

It will be seen that the solar wave-lengths do not show such uniform second differences as are given by the magnesium hydride lines. Various small corrections might be made to bring them into better accordance with the series law, but at least one of them must be of the order of 0·025 tenth-metre, which seems to be too great an error to be attributed to ROWLAND'S relative wave-lengths in so small a region of the spectrum. The series evidence, so far as it goes, is accordingly somewhat against the identification of solar lines with magnesium hydride.

As a result of the whole investigation, it is only possible at present to say that a very small percentage, if any, of the faint lines of the normal solar spectrum are likely to be accounted for by magnesium hydride.

Summary.

(1) No sufficient reason has been found for modifying LIVEING and DEWAR'S conclusion that the spectrum under investigation is produced by the combination of magnesium with hydrogen, and the spectrum has accordingly been referred to throughout as that of magnesium hydride.

(2) The magnesium hydride spectrum exhibits lines at very short intervals from the extreme red to λ 2300, and shows definite groups of flutings having their first head lines in the yellow-green at 5621·57, in the green at 5211·11, in the blue at 4844·92, in the violet at 4371·8, and in the ultra-violet near 2430.

(3) From photographs of the magnesium arc in hydrogen, taken with a concave grating of 10 feet radius, the positions of close upon 2000 lines composing the three principal flutings have been determined. The wave-lengths were derived from the interference standards of FABRY and BUISSON, but have been converted to Rowland's scale to facilitate comparison with solar spectra.

(4) Twelve of the series of lines which compose the green fluting have been traced, and it is shown that none of the formulæ which have been proposed are sufficiently general in their application to represent all of these series within the limits of error of measurement. For the longer series the closest approximation is given by HALM'S equation.

(5) The identification of magnesium hydride in the sun-spot spectrum has been fully confirmed, and is clearly demonstrated by photographs which are reproduced.

(6) It is shown that many of the bright interruptions of the dark background of the spot spectrum are not bright lines, but merely clear interspaces between lines or groups of lines in the spectrum of magnesium hydride.

(7) The presence of the magnesium hydride flutings, together with flutings of titanium oxide and calcium hydride discovered at Mount Wilson, accords with the view that spots are regions of reduced temperature, and that their darkness is at least partly due to absorption.

(8) The investigation of the possible presence of lines of magnesium hydride in the

ordinary solar spectrum is for several reasons inconclusive, but there is evidence that very few, if any, of the thousands of faint lines tabulated by Rowland are to be accounted for by this substance.

In concluding this paper, I am anxious to express my indebtedness to those who have rendered assistance in a somewhat laborious investigation. Mr. H. Shaw, A.R.C.S., has made many of the calculations for checking my determinations of wave-lengths, and Mr. A. Eagle, B.Sc., has been especially helpful in the experimental part of the work, which he has carried out with great skill. Valuable assistance was also given by Mr. T. Banfield in preparing the photographs for reproduction.

Description of Table of Wave-lengths.

The wave-lengths are expressed as nearly as possible on the scale of Rowland's "Preliminary Table of Solar Spectrum Wave-lengths." They may be reconverted to the "absolute" scale of Fabry and Buisson, on which they were originally calculated, by *subtracting* 0·22 from 5621 to 5365·1 inclusive, and 0·170 from 5365·1 to 4371.

In the column headed "Int." (intensity), the brightest lines are represented by 10 and the fainter lines by numbers ranging down to 1, while the faintest lines, as in Rowland's tables, are denoted by 0, 00, and 000. The letter "n," following the intensity number, indicates that the line is unusually nebulous or diffuse, while "s" indicates that the line is of more than average sharpness; d ? indicates that the line is probably double, though not clearly measurable as such. Some of the lines marked "n" may possibly also be double.

In the table referring to the green band, the letters α, β, &c., indicate the lines which are probably associated in the respective series.

It should be noted that some of the magnesium hydride lines may be masked by the ordinary arc and spark lines of the metal magnesium which appear on the plates from which the wave-lengths were determined, namely: the arc lines 5528·641, 5183·791, 5172·856, 5167·497, 4703·177, 4571·275, and the enhanced line 4481·31.

YELLOW-GREEN FLUTING.

λ.	Int.	λ.	Int.	λ.	Int.	λ.	Int.	λ.	Int.
5621·57	1	5618·69	1	5614·54	0	5604·73	1	5599·17	1n
21·22	1	18·23	00	13·66	1	04·14	1	98·76	0n
20·92	1	17·73	1	13·11	1	03·56	00	98·08	0
20·54	2n	17·16	1	11·04	1	01·70	00	97·31	1n
20·38	0	16·48	0	10·48	1	01·05	1	97·01	1n
19·76	2d ?	15·86	1	08·05	1	5600·50	1	96·44	2
5619·23	0	5615·30	1	5607·48	1	5599·90	00	5595·33	1

Yellow-Green Fluting (continued).

λ.	Int.	λ.	Int.	λ.	Int.	λ.	Int.	λ.	Int.
5594·50	1n	5555·81	00	5520·77	1	5491·32	1	5460·95	00
92·89	2	55·29	00	20·39	0	90·53	1	60·34	000
92·59	0	54·34	1	20·32	2	89·34	00	59·41	1n
92·15	2	53·76	1	19·93	0	88·96	1	58·88	0n
92·05	0	53·28	00	18·98	1	88·63	0	58·23	0n
90·74	00	52·24	00	18·59	2	88·55	2	57·98	0
90·14	2	51·86	00	17·82	00	87·93	2	57·58	0
89·53	2	51·32	2	17·17	0	87·55	2	57·22	00
88·83	00	50·92	4	16·64	1	86·99	0n	56·61	1
87·77	1	50·42	00	16·23	2	86·52	0n	56·32	1
87·12	2	49·79	1	15·77	3	86·12	0	56·15	2
86·55	2	49·06	1d?	15·40	00	85·78	1	55·85	0
85·29	0n	48·37	00	14·81	00	85·06	0	55·19	00
83·75	2	47·53	1	14·31	0d?	84·92	0	54·57	1
83·22	2	47·16	0	13·52	00	84·41	0d?	54·36	2
82·61	1	46·67	0n	13·00	0	83·65	1	53·96	1
82·05	1	46·38	0n	12·80	0	83·31	00	53·22	00
81·43	00	45·79	0	12·46	1	82·57	4	52·47	1
80·70	00	45·43	2	12·02	00	82·21	2	52·07	2d?
80·08	2	45·01	2	11·59	3	81·93	0	51·90	0
79·56	2	44·86	0	11·37	2	80·24	0	51·38	00
77·07	0	44·23	0	11·24	2	79·45	2	51·22	2
76·49	00	43·76	2n	10·95	4	79·02	5d?	50·78	1
76·05	2	43·05	0	10·46	00	78·42	0	50·58	0
75·57	2	42·93	1d?	09·70	1	78·06	0	49·74	1
75·35	00	42·58	00	09·14	1	77·53	0	49·27	1
74·54	00	42·22	1	08·35	000	76·74	00	48·67	00
73·73	1	41·45	2n	07·28	0	75·97	1	48·17	1
72·39	00	40·72	1	06·74	1	75·56	1	47·59	4
71·74	2	40·15	0	06·25	2	75·15	3	46·55	1
71·25	3	39·86	000	06·01	00	74·65	1	46·14	1
70·72	1	39·27	1	05·79	3	74·22	00	46·00	0
68·32	2	38·81	4	04·57	00	72·79	00	45·53	1d?
67·70	3	38·65	1	04·20	00	72·06	1	45·08	2
67·13	3	38·12	2	04·03	3	71·50	1	44·94	0
66·90	1	36·57	00	03·64	3	70·97	1	44·00	1n
66·65	2	35·74	3d?	02·70	000	70·68	1	42·98	1
66·38	0	35·16	2	01·99	00	70·36	3	42·59	1
65·72	1n	34·24	000	01·53	00	69·75	0	42·20	0
65·06	1n	33·83	1s	00·78	3	69·00	2	41·74	0
64·43	00	33·28	1	5500·33	4	68·85	2	40·89	0n
64·13	1	32·79	1	5499·66	0	68·64	2	40·45	00
63·61	1	32·44	4	99·28	00	68·35	00	39·97	0
62·76	1	31·95	1	98·81	0	66·51	1	39·50	2n
62·17	4	30·30	00	98·11	000	66·00	1	39·09	5
61·70	3	27·66	00	97·72	0n	65·80	00	38·48	3
61·08	00	26·70	0n	97·40	1n	65·14	0n	38·12	2
60·77	00	26·05	2	97·00	0n	64·87	0n	37·37	000
59·95	1	25·62	2	96·06	1	64·35	2	36·19	0n
59·42	1	25·00	2	95·67	4	64·08	1	35·78	0n
58·48	00	24·49	2	95·15	0	63·75	1	35·30	0n
57·82	00	24·17	1	95·05	1	63·38	1	34·75	00n
57·33	0	23·22	1	94·59	2	62·30	00	34·31	00n
56·89	1	22·73	0	93·65	2	61·74	5d?	33·21	3
56·75	1	21·89	00	92·98	0n	61·39	3 } d?	32·87	4d?
5556·43	3	5521·22	00	5492·70	1	5461·28	3 }	5432·29	00

Yellow-Green Fluting (continued).

λ.	Int.	λ.	Int.	λ.	Int.	λ.	Int.	λ.	Int.
5431·96	0d ?	5401·65	0	5368·96	000	5335·05	0	5297·46	00
31·63	0	01·28	1	67·43	0	34·26	2d ?	96·52	00
31·05	1s	01·12	2	66·85	0	32·86	0	95·27	00
30·54	0	5400·53	0	66·36	00	32·44	00	94·74	0
30·15	1	5399·62	0	65·92	1	31·78	00d ?	93·98	00
29·78	1	98·96	00n	65·65	0	31·25	0	93·34	00
29·39	1	98·54	0	65·29	0	31·04	1	92·97	0n
28·82	0	98·04	1	65·17	0	30·59	00	92·26	0
26·66	2	97·36	3	64·17	1	29·84	2	91·81	000
26·22	1	97·02	1	63·71	2	29·31	1	91·48	2s
25·54	1	95·80	1	63·31	00	28·60	00	91·18	1
24·98	0	95·36	0n	62·92	1	28·37	00	90·06	00n
24·61	0	95·16	00	62·47	0	27·72	00	89·59	00n
24·07	0d ?	94·08	2	61·96	0	25·41	0n	88·54	00n
23·17	1	93·65	3	61·44	00	24·88	00	88·16	0
22·78	1	93·53	0	60·89	0	24·40	0n	86·80	00n
22·15	1	93·05	0	60·37	1n	24·04	1n	86·02	00n
21·55	3	92·62	00	57·95	0	23·62	0	84·96	00n
21·40	3	91·59	1	57·64	00	21·97	0	84·17	0
21·16	1s	91·21	1nd ?	57·36	0	21·33	2	83·70	00
20·90	0s	91·07	00	56·71	0n	20·81	0	83·27	00
20·23	00	90·40	00	55·61	2	20·35	1	82·88	1
19·53	1	89·78	1	55·06	1	19·60	00	82·51	00
19·36	1	89·31	2	54·67	1	18·82	000	81·43	00
19·14	0	88·84	1n	54·27	0	16·51	0n	80·91	1
18·48	00	88·73	00	54·05	1	16·15	0n	80·52	0
17·45	0	87·80	1n	53·72	0	15·62	00	80·05	000
17·28	0	87·28	0	53·48	0	15·03	00	79·85	0
16·85	0d ?	85·58	00	53·18	0	14·11	00	79·35	00
16·42	1	85·05	0	50·65	00	12·79	2	78·68	0n
15·96	00	84·78	1	50·00	0	13·30	1	77·87	00
15·12	0	84·37	2s	49·41	1	12·63	00	77·00	0n
13·46	00	83·96	1	49·00	00	11·38	00	74·41	00
12·97	1	83·42	0	48·50	1	11·01	00	73·40	0
12·57	5d ?	83·00	0	47·78	00	10·70	0	73·00	0
12·19	3	82·36	0	46·79	0	10·13	00n	72·36	0
11·71	00	81·64	0	46·38	2s	09·58	000	71·91	00
11·00	1n	80·99	0	45·66	1n	08·75	1	71·05	1
10·24	0n	80·56	1	44·48	1n	08·50	1	69·71	0
09·95	0n	79·86	00	44·02	2	08·15	00	69·40	1
09·57	1	78·70	00	43·50	1	07·48	0n	68·84	00
09·14	2	78·06	1	42·93	1	06·76	0n	67·84	00
08·66	1	77·65	00	42·70	1	06·18	00	67·43	0
08·05	000	76·72	3	42·30	1	05·50	00	66·93	00
07·45	00	76·31	3	41·20	1s	05·21	00	66·17	000
07·09	1	74·73	0	40·72	000	04·75	00	64·44	000
06·64	00	74·51	0	40·31	00	03·87	00	64·33	0
06·47	1	74·10	3	39·52	0n	02·94	00	62·59	0
05·54	00	73·39	000	39·16	0n	02·48	00	61·87	00
05·17	2	72·27	1	38·43	1n	01·62	0	58·15	0
04·75	1	71·90	0	38·07	0	01·17	00	57·76	0
04·25	0	71·27	1	37·70	1s	00·47	0n	57·01	00n
03·58	3d ?	70·43	1	37·27	00	5300·22	0n	56·65	00n
03·14	2	69·92	1	36·80	00	5299·56	00	55·96	0
02·44	0n	69·81	1	36·34	0n	99·00	0	55·50	00
5401·98	0	5369·25	0	5335·60	00	5298·08	00	5254·79	00

Yellow-Green Fluting (continued).

λ.	Int.	λ.	Int.	λ.	Int.	λ.	Int.	λ.	Int.
5254·29	00	5244·69	00	5233·19	1n	5223·43	1n	5214·86	00
53·84	00	44·00	00	31·54	0	22·66	00	14·31	00
53·11	00	42·08	0n	30·35	0	21·23	000	13·74	0
52·86	0	41·62	00	29·59	0	19·51	0n	13·20	000
52·40	00	41·08	00	28·41	0	18·82	00	12·98	1
50·60	1s	40·35	0	27·34	00	18·33	1	5212·75	00
49·67	1n	39·65	0	26·82	0s	17·30	000		
47·64	00n	37·63	0n	26·17	00s	16·74	000		
46·54	00	36·04	00n	25·62	00	16·29	00		
5246·00	1s	5235·07	00	5224·77	000	5215·85	0n		

Green Fluting.

λ.	Int.	Series.	λ.	Int.	Series.	λ.	Int.	Series.	λ.	Int.	Series.
5211·115	5	α	5199·774	4	γ	5182·149	4	ϵ	5172·312	0	
10·889	5	α	99·009	3	α	81·909	2		72·079	2	
10·582	5	γ	98·795	1	δ	81·687	2		71·715	1	
10·405	7	αβ	98·510	3	β	81·430	3	ζ	71·181	9	ϵ
09·940	6	βγδ	97·571	4†	γ	81·360	3†		70·766	8†	ζ
09·755	4	α	96·628	3	α	81·062	1		70·269	1n	
09·352	3	δ	96·371	0	δ	80·764	7	ϵ	69·635	1n	
09·280	3	β	96·130	3	β	80·540	1†		68·734	8	ϵ
09·073	2	γ	95·208	3	γ	80·162	7	ζ	68·328	8	ζ
08·865	3	α	94·038	3	α	79·937	00		68·011	1	
08·495	3	δ	93·548	3	β	79·718	0n		67·22	1	
08·382	3	β	92·771	2	γ ?	79·577	0n		66·104	8	ϵ
08·045	3	γ	92·04	00n		79·207	7	ϵ	65·716	8	ζ
07·761	3	α	91·246	3	α	78·920	0		65·39	00	
07·444	3	δ	90·736	3	β	78·653	7	ζ	65·08	0	
07·272	3	β	90·403	1	γ ?	78·364	0		63·792	3	
06·793	3	γ	89·51	0n		78·221	0		63·300	8	ϵ
06·442	3	α	89·17	00n		78·00	00		62·920	8	ζ
06·165	2	δ	88·228	3	α	77·762	1		62·01	00	
05·946	3	β	87·730	2	β	77·476	8	ϵ	61·65	0	
05·328	4	γ	87·258	3†		76·975	8	ζ	61·20	0	
04·905	3	α	86·587	3†		76·298	3†		60·324	8	ϵ
04·665	2	δ	85·914	4		75·98	1 } d ?		59·944	8	ζ
04·404	3	β	85·582	00		75·91	1		59·431	3	
03·667	3	γ	85·196	5	ϵ ?	75·556	8	ϵ	58·781	3	
03·159	3	α	84·994	2	α	75·371	00		58·485	1	
02·922	2	δ	84·480	1	β	75·087	8	ζ	57·751	3	
02·638	3	β	84·325	5	ϵ ?	74·817	1		57·163	8	ϵ
01·823	4	γ	83·364	4	ϵ	74·617	2		56·806	8	ζ
01·192	3	α	82·948	00		74·166	1		56·492	1	
00·970	1	δ	82·532	3	ζ	73·460	8	ϵ	56·22	00	
5200·687	3	β	5182·463	3		51(73·020)	(8)*	ζ	5155·910	4	

* Masked by the magnesium line b_2, but interpolated from series relation.

† The intensities of these lines are slightly increased by "ghosts" of the *b* lines.

Green Fluting (continued).

λ.	Int.	Series.	λ.	Int.	Series.	λ.	Int.	Series.	λ.	Int.	Series.
5155·60	0		5134·390	5	ζ	5116·162	2		5093·759	2	σ
55·319	2		33·747	3	κ	15·204	1		92·750	3	
55·048	2		33·353	4	μ	14·740	3	ρ	92·310	3	
54·879	4n	κ	33·018	2	ρ	14·208	4	σ	91·840	3	κ
54·684	1		32·69	00		13·747	1		91·479	3	μ
54·365	3		32·330	2	σ	13·317	4	η	90·907	4	ϵ
54·284	3		32·007	1		13·140	2	κ	90·549	4	ζ
54·009	2	μ	31·82	0		12·832	5	μθ	90·21	00	
53·826	7†	ϵ	31·385	1		12·330	1		89·98	0	
53·470	7	ζκ	31·136	1		11·793	5	ϵ	89·66	00	
53·14	00		30·707	3	κ	11·462	5	ζ	89·383	4	η
52·786	3	μ	30·436	6	ϵ	11·176	2		88·894	5	θ
52·37	0		30·323	2	μ	09·803	2	ρ	88·80	3	ρ
52·043	2		30·073	5	ζη	09·228	4d?	κσ	88·33	1	σ
51·964	2	κ	29·992	1		08·830	4	μ	87·97	0n	
51·62	00		29·68	00		08·433	2		87·41	00	
51·355	3	μ	29·495	4	θ	08·23	00		87·18	3	κ
50·909	1		29·257	0		07·527	5	η	86·84	3	μ
50·309	10	ϵκ	29·065	0		07·041	3	θ	86·05	1	
49·976	4	ζ	28·77	0		06·759	3	ϵ	85·57	0	
49·688	5n	μ	28·646	1n	ρ	06·422	3	ζ	85·365	3	ϵ
48·927	1d?		28·280	1		05·899	2		85·03	2	ζ
48·433	3	κ	28·040	1	σ	05·52	1		84·83	2	
47·925	3	μ	27·78	00		05·050	3	κ	84·10	0	
47·638	1		27·512	3	κ	04·720	4	μρ	83·40	0	
47·09	2n		27·120	5	μ	04·250	2	σ	83·140	5	ηρ
46·689	7	ϵ	26·81	0		03·98	0		82·682	5	θσ
46·359	7	ζκ	26·36	1n		03·56	0		82·37	2	κ
45·938	3	μ	26·003	4	ϵ	03·36	0		82·02	2	μ
45·52	00		25·664	5	ζ	02·836	3		81·54	0	
45·368	5		25·32	000		02·456	2		81·26	3	
45·14	00		25·20	000		02·13	0		80·89	3	
44·840	4		24·738	1		01·84	0		80·34	0	
44·196	6	κ	24·547	2	η	01·590	7	ϵη	80·06	00	
43·780	4	μ	24·26	00		01·240	4	ζ	79·700	3	ϵ
43·31	00		24·135	9	κθρ	01·126	3	θ	79·390	3	ζ
42·868	7	ϵ	23·790	2	μ	00·800	2	κ	79·02	1	
42·511	6	ζ	23·560	2	σ	5100·433	2	μ	78·21	0	
41·862	4	κ	22·965	3		5099·99	0		77·95	00	
41·438	4	μ	22·436	3		99·72	00		77·50	3	κρ
41·22	0		22·03	00		99·576	3	ρ	77·091	4	μσ
40·376	5		21·57	00		99·204	2		76·755	4	η
39·874	4		21·404	4	ϵ	99·06	2	σ	76·295	4	θ
39·316	4	κ	21·046	5	ζ	98·39	1		76·09	0	
38·885	8	ϵμ	20·644	3	κ	97·99	0		75·54	1	
38·537	6	ζ	20·277	3	μ	97·05	1		75·15	0	
38·19	00		19·92	0		96·335	7	ϵκ	74·20	00	
37·64	00		19·515	2	ρ	95·990	5	ζμ	73·940	3d?	ϵ
37·193	3n		18·975	8	ησ	95·548	3	η	73·597	2	ζ
36·615	5	κ	18·510	6	θ	95·32	0		73·35	00	
36·213	5	μ	17·65	0		95·069	4	θ	72·99	1n	
35·86	00		16·963	3	κ	94·78	0		72·58	1n	
35·255	5		16·636	7	ϵμ	94·51	0		72·41	1n	κ
5134·755	9	ϵ	5116·327	3	ζ	5094·207	2	ρ	5072·01	2	μ

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† The intensities of these lines are slightly increased by "ghosts" of the *b* lines.

Green Fluting (continued).

λ.	Int.	Series.	λ.	Int.	Series.	λ.	Int.	Series.	λ.	Int.	Series.
5071·76	2	ρ	5048·00	0		5025·77	000		5000·46	2	
71·31	2	σ	47·60	2	ρ	25·42	000		00·17	0	
71·08	0		47·19	2	σ	24·97	000		4999·81	0	
70·60	1		46·94	00		24·03	1	ε	99·64	0	
70·28	3	η	46·49	1		23·60	0	ζ	99·05	0	
69·81	3	θ	46·17	0		23·52	0		98·69	000	
69·27	1		45·72	0d ?		23·18	1		98·23	00	
68·60	1		45·36	0		22·62	3	η	97·90	00	
68·18	1		44·99	0		22·12	3	θ	97·44	00	
68·066	2	ε	44·58	0		21·70	1		96·94	0	
67·713	1	ζ	44·32	1		21·40	000		96·76	1	
67·21	1n	κ	44·00	0		20·72	1		96·39	000	
66·86	1n	μ	43·500	4	εη	20·37	1		95·93	000	
66·13	00		43·052	3	ζθ	19·60	00		95·46	3	
65·88	3	ρ	42·14	00		19·05	0		95·03	3	
65·44	3	σ	41·69	1		18·65	1		94·51	000	
65·00	0		41·34	2	ρ	18·45	000		94·31	00	
64·50	0		40·94	2	σ	18·17	000		93·97	2	η
64·01	1		40·53	0		17·95	1		93·53	2	θ
63·697	3	η	40·34	0		17·52	1d ?	ε	92·56	0n	
63·255	2	θ	39·98	000		17·09	0	ζ	92·04	0n	
62·63	00		39·63	2		16·54	000		90·71	000	
62·39	1		39·31	2		16·00	0		90·15	0	
62·06	1	ε	38·89	00		15·53	3	η	89·70	1d ?	
61·94	2	κ	38·47	1		15·10	3	θ	89·28	0	
61·66	1n	ζμ	37·62	1		14·73	0		88·82	1	
60·63	1		37·07	2	ε	14·04	00		88·46	1	
60·19	1		36·67	1	ζ	13·59	00		88·04	00	
59·870	2	ρ	36·61	3	η	13·21	2		87·89	000	
59·436	3	σ	36·15	2	θ	12·74	00		87·27	0	
59·10	1		35·86	00		12·32	1		86·91	00	
58·71	0		35·45	00		11·94	1		86·68	2	η
58·44	0		35·07	1	ρ	11·68	00		86·24	2	θ
58·13	0		34·70	1	σ	10·88	00		84·95	00	
57·80	00		34·43	0		10·67	0	ε	84·03	1d ?	
57·41	00		33·77	1		10·30	00	ζ	83·59	00	
57·060	4	η	33·62	0		09·82	2		83·16	00	
56·580	4	θ	33·43	0		09·42	00		82·97	0	
56·16	1		32·97	1n		09·01	2		82·50	00	
56·00	1	ε	32·46	1n		08·63	1		82·22	1	
55·60	1	ζ	32·16	1		08·39	2	η	81·92	1	
55·24	0		31·68	1		07·93	2	θ	81·69	0	
54·81	1n		31·38	00		07·42	000		81·32	00	
54·48	1		31·02	00		06·89	00		80·75	00	
54·15	0		30·61	1	ε	06·53	0		79·97	000	
53·79	2	ρ	30·25	1	ζ	06·14	0		79·36	2	η
53·36	2	σ	29·65	3	η	05·41	0		78·94	2	θ
53·20	0		29·17	3	θ	04·25	0		78·07	00	
52·60	00		28·54	1n	ρ	03·91	0	ε	76·88	0n	
52·03	00		28·13	0	σ	03·57	0	ζ	76·43	00	
50·92	1		27·85	0		03·14	2		76·09	00	
50·66	1		27·51	0		02·72	0		75·72	000	
50·320	3	η	27·28	00		01·68	00		75·10	1	
49·810	5d ?	εθ	26·92	000		01·41	2		74·40	00	
49·419	2	ζ	26·53	2		01·23	2	η	74·25	0n	
5048·81	00		5026·12	1		5000·70	2	θ	4973·83	000	

Green Fluting (continued).

λ.	Int.	Series.	λ.	Int.	Series.	λ.	Int.	Series.	λ.	Int.	Series.
4973·36	000		4955·52	1		4930·36	00		4897·60	000	
72·51	000		54·93	00		29·84	00		96·78	000	
71·97	2	η	54·37	000		29·36	00		95·33	0n	
71·55	2	θ	53·17	000		27·69	0		94·73	00	
70·88	0n		52·48	00n		25·89	0		91·11	00	
70·54	000		51·96	00		25·21	0d ?		90·16	0	
70·18	0		51·38	00		24·73	0		88·05	0	
70·08	0		50·74	2		23·32	1		87·47	0	
69·61	0		49·84	000		22·55	0		86·05	00	
69·38	00		48·64	00		21·38	00		85·15	00	
69·11	00		47·72	00n		20·30	1		84·39	000	
68·74	0		46·72	00n		19·97	0		83·89	000	
68·57	00		46·38	00		19·66	00		83·75	0	
68·01	2d ?		45·90	0		19·26	0		83·34	00	
67·58	0		45·36	0d ?		19·03	0		80·79	00	
66·99	00		44·93	00		18·71	0		76·50	0	
66·04	00		44·10	0		17·09	000		75·45	00	
65·41	000		43·42	000		16·19	000		74·90	00	
65·25	00		42·80	0		15·70	00		74·64	0	
64·66	2	η ?	42·48	1		15·30	00		74·03	000	
64·24	2	θ ?	42·09	1		15·16	0		73·50	000	
64·06	0		41·36	0		13·68	00		72·56	00n	
63·45	0n		40·33	0		13·39	1		71·63	1	
63·29	0n		39·99	0		13·13	0		71·04	000	
62·80	0		39·13	0		12·33	000		70·41	0	
62·09	00		38·61	0		06·88	000		61·93	000	
61·72	00		37·85	00		06·57	0		60·49	00n	
61·48	1		37·02	000		06·27	000		60·08	00	
61·19	1		36·59	0		04·99	1		59·16	00	
60·45	000		36·39	000		04·60	0		54·90	000	
59·88	00		36·06	0		02·85	0		50·41	0n	
58·92	000		35·93	000		02·20	1d ?		48·08	00	
58·50	00		35·19	1		01·57	0		47·65	00	
57·92	1		34·79	2		4900·69	0d ?		46·38	00	
57·76	0		33·91	0n		4899·97	000		45·78	00n	
57·32	1	η ?	33·07	0n		99·32	0		4845·27	0	
56·93	1	θ ?	32·52	0n		98·62	1				
4956·29	000		4930·95	0n		4898·40	0				

BLUE FLUTING.

λ.	Int.	λ.	Int.	λ.	Int.	λ.	Int.	λ.	Int.
4844·92	2	4842·15	2	4838·86	0	4836·68	0	4833·54	0
44·65	3d ?	41·88	2	38·56	3	36·30	1	33·31	0
44·27	0	41·50	0	38·26	0	36·04	3	33·11	2
44·00	0	41·11	1	38·01	00	35·92	1	32·93	0
43·67	2d ?	40·68	1	37·83	1	35·44	3	32·66	0
43·19	2	40·28	1	37·50	00	35·01	0	32·26	1
42·69	0	39·80	1	37·09	4	34·52	3	31·89	0
4842·56	1	4839·30	2	4836·85	00	4834·06	3	4831·57	1

Blue Fluting (continued).

λ.	Int.	λ.	Int.	λ.	Int.	λ.	Int.	λ.	Int.
4831·12	2	4810·40	0	4787·91	1	4770·40	1	4748·13	1 } d?
30·76	1	10·19	1	87·65	1	70·11	3	48·02	1 }
30·46	00	09·74	1	87·31	0	69·79	1	47·59	1
29·97	5	09·04	0	87·07	1	69·42	1	47·38	00
29·55	3	08·67	1	86·76	1	69·00	1	47·19	1
29·14	00	08·10	1	86·51	2	68·51	0	46·36	00
28·78	3	07·78	0	86·28	1	68·26	2	46·12	0
28·55	00	07·00	3	85·89	1	68·02	1	45·86	2
28·31	2	06·26	1n	85·59	1	67·52	0d?	45·42	1
28·03	0	05·85	1	85·23	3	67·05	1	44·31	1
27·77	1	05·54	0	85·00	0	66·81	2	43·97	1
27·45	1	05·14	0	84·73	0	66·49	2	43·11	1
26·96	2n	04·79	0	84·46	3	66·14	1	42·87	00
26·47	2	04·31	1	84·06	3	65·76	00	42·58	0
26·10	0	03·76	2	83·72	1	65·24	1	42·23	1
25·98	2	03·45	1	83·29	2	65·07	0	41·90	2
25·76	0	03·10	1	82·95	1	64·69	2	41·22	0
25·51	0	02·63	3	82·53	1	64·36	00	41·02	1
25·19	0	02·41	0	82·12	1	63·94	1	40·68	3
24·72	3n	02·13	3	82·01	2	63·65	1	40·41	0
24·37	1	01·87	0	81·87	1	63·37	2	39·83	1
24·09	0	01·53	4	81·42	1d?	62·96	0n	38·99	00
23·79	0	00·97	3	81·06	0	62·56	1	38·66	1
23·12	2	00·43	1	80·86	2	62·45	0	38·25	1
23·00	2	4800·25	1	80·50	2	61·84	2	37·76	2
22·66	1	4799·73	2	80·24	0	61·23	0	37·43	0
22·54	00	99·49	3	80·03	2	60·93	0	37·17	0
22·16	0	99·03	1	79·65	1	60·66	1	36·62	00
21·77	3	98·62	3	79·55	1	60·21	1	36·33	0
21·51	1	98·22	3	79·26	1	59·95	0 } d?	35·79	0
21·22	00	97·74	3	79·13	1	59·83	0 }	34·99	0
21·07	0	97·35	3	78·86	0	59·47	2	34·85	0
20·63	0	96·76	3	78·56	2	59·21	0	34·62	1
20·44	0	96·37	3	78·17	2	58·91	0	34·31	1
19·87	5d?	95·99	00	77·79	2d?	58·23	00	33·83	00
19·60	0	95·70	4	77·43	0	57·49	2	33·30	0
19·33	1	95·32	4	77·00	0	57·06	2	33·04	00
18·92	00	94·87	1	76·82	5	56·45	3	32·58	0
18·49	0	94·61	1d?	76·60	0	56·02	2	31·95	1
18·27	0	94·32	5d?	76·30	1	55·75	0	31·46	2
18·01	2	93·85	0d?	76·14	0	55·40	0	31·03	1n
17·51	1	93·42	0	75·84	0	54·63	00	30·56	0
16·67	2n	93·28	3d?	75·48	3	54·22	00	30·23	00
16·17	4	92·72	2	75·07	2d?	54·00	1	29·97	0
15·56	0	92·55	00	74·57	1	53·57	3	29·31	0
15·02	1	92·22	3	74·26	1	53·10	1	29·16	0
14·51	0	91·93	3	74·04	0	52·93	1	28·82	0n
14·26	1	91·51	1	73·71	2	52·54	1	28·63	00
14·07	0	91·24	1	73·45	2	52·02	0n	28·15	00
13·61	1	90·97	2	73·08	1d?	51·42	2	27·82	00
13·30	1	90·45	1	72·65	3	50·85	2	27·42	1
12·74	1	90·01	1	72·34	0	50·66	0	26·95	2
12·15	1d?	89·59	4	71·92	0	50·41	1	26·79	00
11·70	0	89·24	1d?	71·58	1	49·37	1	26·38	1
11·51	1	88·66	2	71·23	2	48·98	1	24·61	0
4810·89	1	4788·23	4	4770·85	1	4748·64	0	4724·30	3

Blue Fluting (continued).

λ.	Int.	λ.	Int.	λ.	Int.	λ.	Int.	λ.	Int.
4723·93	1d ?	4694·57	0	4643·57	1	4554·26	1	4483·21	1n
23·20	00n	93·92	0	42·10	00	51·49	1	80·38	2
22·38	0	93·30	00	41·19	1	50·36	00	78·78	2
21·16	0	92·92	00n	40·36	0	46·66	0	76·61	1
20·97	1	92·68	0n	39·78	1	44·41	1	75·47	5
20·69	0	92·13	00	39·05	0	44·22	1	74·76	0
20·36	0	91·22	0n	35·10	0	42·73	2	73·83	00
20·00	00	90·90	00	34·13	00	42·05	00n	73·21	1
19·58	00	90·58	0n	33·84	1	41·31	00	70·91	1
19·24	1	90·16	0	33·12	00	40·25	00	70·16	00
18·48	0	89·78	00	32·47	0	39·47	00	69·61	1
18·23	0	88·76	00	31·08	1	37·53	1d ?	66·75	1
17·97	0	88·20	00	28·98	0	35·00	0	64·35	0
17·80	0	87·67	1	28·60	0	34·40	0	63·44	1
17·38	0	87·21	00	25·33	0	33·95	1	61·03	1
17·04	1	86·87	0	24·64	0	31·98	2	60·49	0
16·58	2	86·71	0	24·15	1	30·46	2	58·97	1
15·89	1	86·27	0	23·69	00	29·49	00	58·28	1
15·74	0	86·00	0	22·95	0	25·65	00	55·62	0
14·97	00	85·73	0	21·78	1	23·31	1	52·92	0
14·47	00	85·13	00	18·70	0	20·67	2	51·62	00
13·85	1n	84·64	00	14·47	1	20·31	0	51·18	1
13·48	1	83·60	1	11·16	00	19·63	1	50·63	0
13·14	0	83·18	0n	10·20	0	19·18	1	50·19	00
12·19	00n	82·80	00	09·37	0n	17·85	0	47·56	1
11·68	00	82·52	0n	08·28	00	17·31	0	45·65	0
11·37	00	81·62	1	07·55	0	16·70	1	44·82	1
10·93	0	80·53	1	07·00	0	16·41	00	42·22	0
10·37	00	78·50	00n	06·46	0	15·94	1	41·88	0
09·90	1	75·70	1	05·86	1	14·93	00	40·63	00
09·58	0	75·05	00	03·60	1	14·46	00	40·16	00
09·08	1	74·49	1	03·19	00	13·85	1	35·90	1
08·40	1	73·48	00	02·91	00	13·34	1	32·91	0
07·82	1	73·26	00	4600·52	0	11·28	0	30·71	0n
07·31	0	72·43	00	4598·04	0	10·55	2	30·47	0n
06·93	0	67·61	0	94·20	0	09·18	1	29·70	1
06·44	1	67·44	00	93·02	0n	08·91	1	27·24	0n
06·17	1	66·75	0	90·55	00	06·61	00n	23·77	0
05·76	00	65·80	0	89·85	0	04·41	00	23·28	1
05·38	0	64·92	1	88·75	1	03·70	0	22·34	1
05·10	1	64·19	1	87·13	00	02·02	0	20·70	1
04·62	0n	63·80	0	86·61	1	01·50	2	19·42	0
02·71	0	62·88	00	84·56	0	4500·31	1	18·88	0
02·16	0	62·52	00	82·64	1	4499·63	00n	15·64	0
01·60	0	61·81	1	78·98	0	99·19	00n	14·66	0
01·10	00	59·22	0	77·61	00	98·49	0	14·04	1
00·75	1n	57·62	00	76·92	00n	97·06	2	13·46	1
4700·25	0	56·57	0	75·94	00n	94·95	00	10·26	0
4699·40	1	55·33	1	74·60	00	94·40	00	09·86	1
99·02	00	54·32	0	72·79	1	93·70	2d ?	09·60	00
97·45	0	53·97	00	66·33	0	92·58	1	07·16	1
96·94	0	53·62	00	65·83	00	90·30	2	04·95	1
96·12	0	46·97	1	61·79	00	89·10	1	03·90	1
95·79	00	46·06	0	59·50	1	86·72	1	02·77	2
95·35	00	45·69	0	58·04	1	85·92	2	01·52	0
4694·91	1	4644·54	00	4556·15	2	4485·38	1n	4400·70	1

Blue Fluting (continued).

λ.	Int.	λ.	Int.	λ.	Int.	λ.	Int.	λ.	Int.
4399·80	0	4395·05	00	4388·19	0	4383·79	1	4378·44	0
98·33	1n	94·09	0	87·84	00	83·02	00	78·12	1
98·13	00	93·30	1	87·47	00	80·57	0	73·78	0
96·63	1	90·00	0	86·17	00	80·20	1	72·35	00
4395·99	0	4389·04	1	4385·86	0	4378·98	0	4371·83*	0

* 1st line in violet fluting.

Description of Plates.

General Note.

In the process of enlargement a cylindrical lens has been used to broaden the spectra and smooth out irregularities produced by the grain of the gelatine films. Spurious lines due to grain have been introduced in this way, but they are probably too faint to appear in the reproductions. In case of doubt, comparison with the wave-length catalogue may be made.

PLATE 12.

A.—The first strip shows the three principal flutings of magnesium hydride, as photographed with the small Littrow spectrograph, and indicates their relative intensities more correctly than the other photographs, which have been copied in sections. The remaining strips give a general map of the spectrum from 5622 to 4600, as photographed in the first order of the 10-feet concave grating.

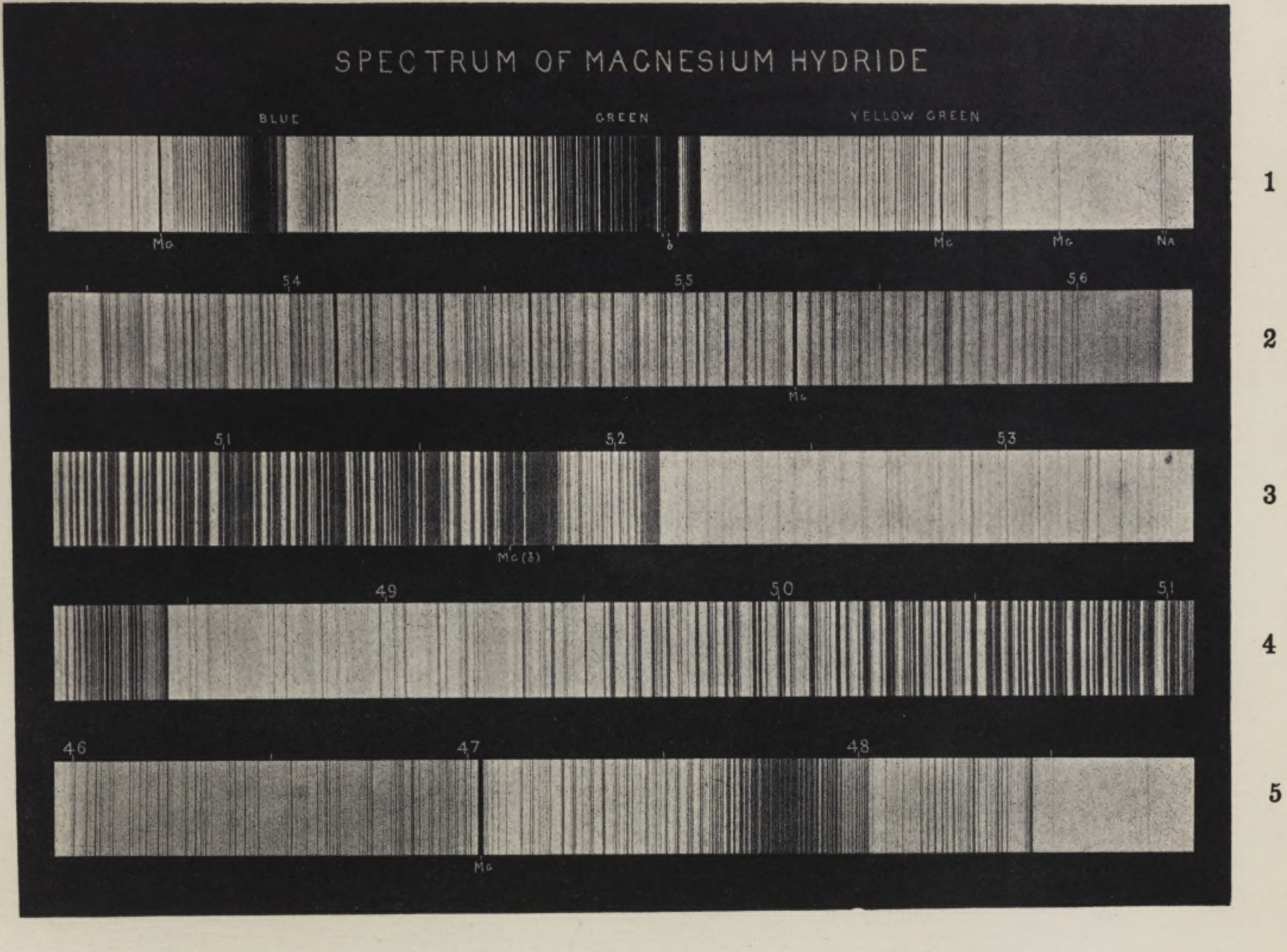
B.—The photographs show the brighter parts of the green fluting, as photographed with the concave grating in the second order. The principal series of lines which compose the fluting are also indicated.

PLATE 13.

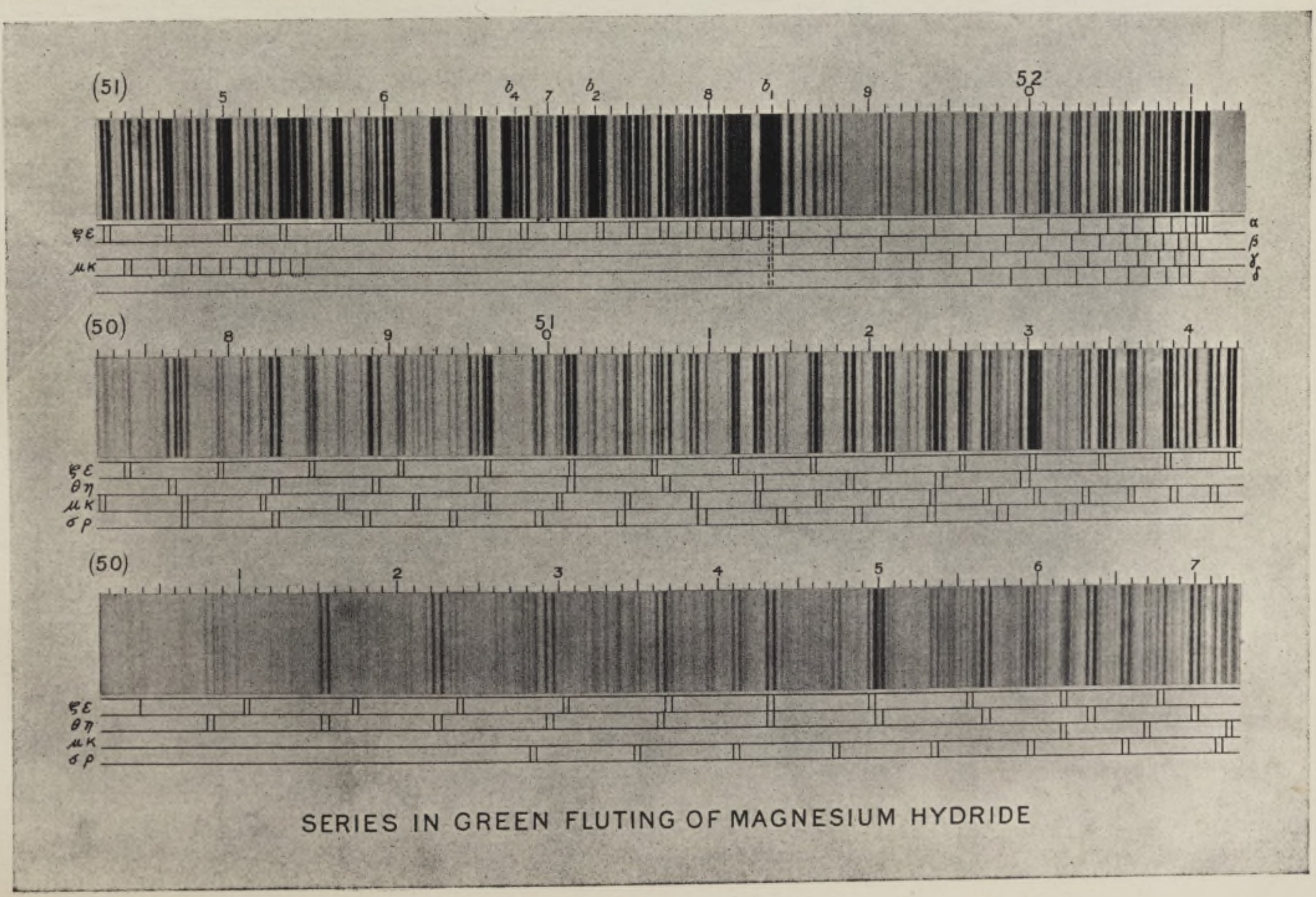
Photographs demonstrating the presence of magnesium hydride in sun-spots. The photographs of the sun and sun-spot spectra were taken by Mr. Evershed at Kodaikanal (the exposure for the sun-spot was about six times that for the solar spectrum).

The lines marked with dots in Plates 12B, and 13 are "ghosts." Other lines affected by ghosts of the *b* group are indicated in the catalogue.

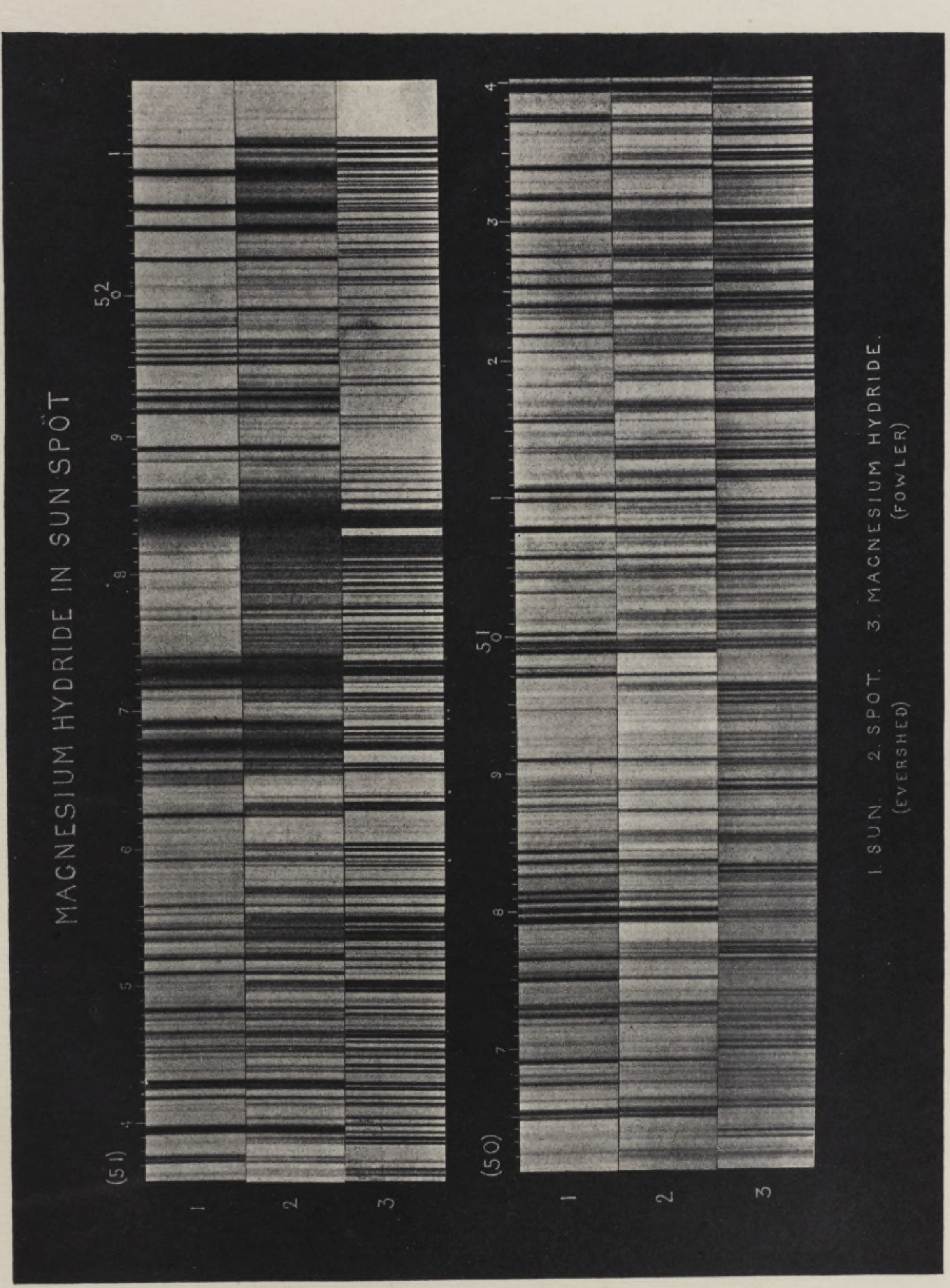
A



B



SERIES IN GREEN FLUTING OF MAGNESIUM HYDRIDE


MAGNESIUM HYDRIDE IN SUN SPOT
1. SUN. 2. SPOT. (EVERSHED) 3. MAGNESIUM HYDRIDE. (FOWLER)
(51)
4
5
6
7
8
9
52
1
(50)
7
8
9
51
1
2
3
4
1
2
3

VI. BAKERIAN LECTURE.—*Series Lines in Spark Spectra.*

By A. FOWLER, *F.R.S., Assistant Professor of Physics, Imperial College, South Kensington.*

MS. received April 20,—Lecture delivered April 2, 1914.

[PLATE 3.]

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Published separately, July 18, 1914.

§ 1. *Introductory.*

The classical work of Rydberg, and that of Kayser and Runge, dealt mainly with series lines in spectra which are developed in the flame or electric arc, or in vacuum tubes with discharges of moderate intensity. The lines to be discussed in the present communication are some of those which belong to the class of *enhanced* lines as defined by Lockyer; that is, they are relatively intensified in passing from arc to spark conditions.

In considering these lines it is necessary to take account of the fact that their behaviour in the arc is different for different elements. At least three classes may be recognised:—(I.) Enhanced lines like the H and K lines of calcium, which are well developed in the ordinary arc; (II.) Lines which only appear with small intensities in the arc, such as the enhanced lines of iron; (III.) Lines which do not appear in the ordinary arc (except very locally near the poles), but are strongly developed under spark conditions, as in the case of the well-known magnesium line at λ 4481.

Until very recently the only evidence that enhanced lines may belong to series was that afforded by Runge and Paschen's observations of the spectra of magnesium, calcium, strontium, barium, and radium, under the influence of a magnetic field. In the case of each of these elements, three pairs of lines of Class I. were observed, and though no series formulæ could be calculated for them, the magnetic resolutions proved that one pair belonged to the Principal series, another to the Sharp, and the third to the Diffuse series. Further discussion of these series has become possible through the valuable work of Lyman in the Schumann region, published in 1912.

The present investigation was undertaken in connection with the new series of lines which were produced in 1912 by passing strong condensed discharges through helium tubes containing hydrogen as an impurity.* These lines, of which the strongest is at λ 4686, are of considerable importance in celestial spectroscopy because of their occurrence in the spectra of some of the nebulæ, and in stars which are generally regarded as representing the earliest stages of stellar condensation. One of the series, only feebly visible, was in apparent agreement with a series of lines first observed in ζ Puppis by Pickering, and attributed to hydrogen because of their simple relation to the Balmer hydrogen series. The other was a strong series, which included the lines assigned by Rydberg to the Principal series of hydrogen from analogy with the spectra of the alkali metals. In addition to the Rydberg lines, however, the "4686" series included intermediate lines, which the then recognised formulæ suggested was a second Principal series related in a simple manner to the first. As the new lines could not be obtained from hydrogen alone, and in consideration of the occurrence of lines not anticipated by Rydberg, it was soon felt that further inquiry should be made as to the value of the numerical evidence on which their assignment to hydrogen was chiefly founded. A search for other series of similar character was therefore undertaken, in the hope that some generalisation with regard to such series might be arrived at.

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* 'Monthly Notices, R.A.S.,' vol, 73, p. 62 (December, 1912).

The mode of production of the "4686" lines suggested spark spectra as the most promising source of such series, and, shortly afterwards, experiments on magnesium yielded some new lines of that element which were obviously associated with the spark line 4481 in series of the kind looked for. No satisfactory evidence of relation to other series of magnesium lines, however, was then obtained, and it seemed possible that both the "4686" and the "4481" series were of a new type, having no necessarily simple relation to other known series in the respective spectra.*

The lines of the "4686" and the associated Pickering series have since become of increased importance, in connection with theories of the constitution of the atom, through the theoretical investigations of Dr. BOHR.† Beginning with the "Rutherford" model of the atom, and introducing PLANCK's quantum, Dr. BOHR has derived a formula for the hydrogen spectrum which excludes these lines, while agreeing closely with the hydrogen series about which there can be no doubt. The "4686" and Pickering series, however, are included in another formula, derived for the emission of helium atoms during the first stage of their reformation when both electrons are supposed to have been removed by the strong discharges employed. This formula is identical, in a first approximation, with that for hydrogen except that the Rydberg constant "N" (= 109,675 for ROWLAND's scale) has four times its ordinary value. The two "Principal" series previously assigned to hydrogen were thus united in a single formula and attributed to helium, while the Pickering series was made to include intermediate lines coincident with the Balmer series of hydrogen. As the lines in question, whatever their origin, must be regarded as enhanced lines, it was evidently desirable to continue the general investigation of lines of this class.

Further investigation of magnesium, in particular, was also suggested by the discovery made by PASCHEN,‡ and by KING,§ that the line 4481 is a close doublet ($\delta\lambda$ = about 0·2 Å.U.), as it appeared that a valuable indication of the type of series to which it belongs might be obtained if other members could be resolved. Photographs with high dispersion have accordingly been taken for the resolution of the lines and to provide more accurate data for testing the formula for enhanced lines which was suggested by the work of BOHR. Other photographs, taken with smaller dispersion, have resulted in the detection of additional lines which clearly belong to series related to that beginning with 4481. The discussion of the new data for magnesium, and of the data for calcium and strontium given by other observers, has led to some conclusions which are probably of general application to enhanced line series.

The chief results of the investigation are summarised in § 14.

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* 'Roy. Soc. Proc.,' A, 1913, vol. 89, p. 133.

† 'Phil. Mag.,' vol. 26, p. 1 and p. 476 (1913).

‡ Communicated privately (1913, August).

§ 'Astrophys. Jour.,' vol. 38, p. 327 (1913).

§ 2. *Wave-lengths of the* "4481" *Series of Magnesium.*

The members of the "4481" series are essentially spark, or enhanced lines, but they are most conveniently produced in an arc between magnesium poles *in vacuo*, and are best observed in the blue green patch in the region of the negative pole, viewed end-on. Under these conditions they are obtained as very narrow lines, well adapted for accurate measurement. The new determinations of wave-lengths have been based as far as possible on the interferometer values for the lines of iron, or upon grating determinations depending upon such standards, among which those given by Dr. KEIVIN BURNS* have been especially useful.

The Line 4481.—Previous photographs taken in the 1st order of a concave grating of 10 feet radius gave no indication of the resolution of 4481, but photographs recently obtained in the 3rd and 4th orders show it to consist of two clearly separated lines (Plate 3, fig. 6), of which the more refrangible is the stronger, as stated by KING. The lines have no close resemblance to the side components of a reversed line, as the space between them is considerably greater than the thickness of either of them, and, as pointed out by KING, the measured separation is the same in photographs taken with different lengths of exposure, and in different orders of the grating. Iron arc comparisons were exposed both before and after the magnesium, and the plates were measured in the usual way with red right and red left. The mean results from numerous measurements are :—

International scale.	Rowland scale.	$\delta\lambda$.
4481·327	4481·495	0·198
4481·129	4481·297	

Dr. KING's values for the two components on ROWLAND's scale are 4481·499±0·001 and 4481·284±0·001 ($\delta\lambda = 0·215$), but from the reproductions given in his paper, the lines do not appear to have been as narrow as those from which the above results were obtained.

[*Note.*—The new measurements of λ 4481 as a doublet permits of a more satisfactory conclusion as to its presence among the Fraunhofer lines than has hitherto been possible. ROWLAND tabulates two lines, each of intensity "0" at 4481·298 and 4481·515, with an intermediate titanium line (intensity 1) at 4481·438. The agreement for the stronger component, which is a very distinct line in ROWLAND's map, may be considered exact, but the discordance on the less refrangible line exceeds the probable error of measurement, and the intensity is also a little too high in the sun. It may be, however, that both these discordances are caused by a still fainter solar line which is nearly superposed on that of magnesium, since such lines are very numerous. The presence of Mg 4481 as faint lines in the solar spectrum may therefore be considered very probable, indicating a condition somewhat more advanced than the ordinary arc, in the direction of the spark.]

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* 'Zeitsch. f. Wiss. Photog.,' 1913, XII., 6, p. 219; 'Lick Obs. Bull.,' vol. VIII., No. 247 (1913).

The Line 3104.—This line was easily resolved in the 4th order of the grating (Plate 3, fig. 7), and has two components exactly resembling those of 4481, but separated by less than one-tenth of an Ångström unit. The iron arc comparison was photographed through a glycerine solution of para-nitroso-dimethyl-aniline contained in a quartz cell, as recommended by Prof. R. W. Wood.* This solution absorbs the superposed 3rd order spectrum, but transmits the 4th order lines with reference to which the magnesium lines were measured. The mean results from three excellent plates with five comparison spectra are as follows :—

International scale.	Rowland scale.	$\delta\lambda$.
3104·805	3104·929	0·092
3104·713	3104·837	

The Line 2661.—On the assumption of a constant wave-number interval between the components of the resolved lines, the separation at 2661 would be about 0·07 Å.U. which is very near the limit of resolution of the grating. Hence with the exposures of 3 to 5 hours required in the 3rd and 4th orders, a very slight unsteadiness of conditions, such as might arise from small variations of temperature, would tend to mask any resolution which might otherwise be effected. Many 3rd order plates were taken, all of which show the line broadened, but only one suggests resolution, and on none of the 4th order plates was this result improved upon. Measurements of the best 3rd order plate gave the following wave-lengths :—

International scale.	Rowland scale.	$\delta\lambda$.
2660·821	2660·909	0·066
2660·755	2660·843	

These values are in good accordance with the mean of several determinations from 1st order plates, namely, 2660·785 (I.Å.), 2660·873 (R).

The Remaining Lines.—It has not been found possible to photograph beyond the first three lines in the higher orders of the grating, but the wave-lengths of the next two, 2449 and 2329, have been checked by a photograph in the first order, giving a dispersion of 5·5 Å.U. per mm. Wave-lengths of iron lines given by Burns were used for the line 2449, but were not available for 2329. The lines 2253, 2202, 2166 do not appear on any of the grating photographs, but are well shown on the original plates taken with a quartz spectrograph, giving an average dispersion in this region of about 6 Å.U. per mm. Further measurements have been made, but in the absence of better standards it has not been found necessary to modify the values given in the previous paper. The reference spectrum for these lines was the copper arc, as given by KAYSER and RUNGE, and the lines are subject to an uncertainty of about 0·05 Å.U. in absolute value.

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* 'Phil. Mag.,' Series 6, vol. 6, p. 257 (1903).

All the necessary details with regard to the "4481" series are brought together in Table I., the corrections to vacuum having been made from KAYSER's table.*

TABLE I.—The "4481" Series of Magnesium.

λ, wave-length (I.Å.).	Estimated limit of error in λ.	δλ.	n, wave-number (*in vacuo*).	Estimated limit of error in n.	δn.	Remarks.
4481·327	0·005	0·198	22,308·68	0·025	0·99	From 3rd and 4th order plates.
4481·129	0·005		9·67	0·025		
3104·805	0·005	0·092	32,198·99	0·05	0·94	From 4th order plates.
3104·713	0·005		9·93	0·05		
2660·821	0·01	0·066	37,571·43	0·14	0·94	From 3rd order plate.
2660·755	0·01		2·37	0·14		
2449·573	0·01		40,811·31	0·17		From 1st order plate.
2329·58	0·02		42,913·30	0·4		
2253·87	0·05		44,354·65	1·0		From quartz spectrograph.
2202·68	0·05		45,385·36	1·0		
2166·28	0·05		46,147·86	1·1		

From the separations of the three lines which have been resolved, it appears at once that the interval between the components, in wave-numbers, is sensibly constant, and that the series is therefore not of the ordinary Principal type. In a Principal series having a separation of 0·99 for the first member at 4481, the interval at 3104 would be reduced to 0·64, and at 2660 to 0·44, but there is no evidence of such contraction.

§ 3. *Formulæ for the* Mg "4481" *Series.*

The application to these lines of the ordinary formulæ of RYDBERG, RITZ, or HICKS, requires the division of the lines into two series by taking alternate lines, the two series thus resembling the Diffuse and Sharp series which occur in the spectra of other elements. Two such series can only be included in a single formula in the special case when the fractional terms associated with the parameter m differ by exactly 0·5, the Rydberg constant N being then replaced by 4N, if m takes successive integral values. In the general case, an objection to this combination would be the smaller intensities of the lines of the Sharp as compared with those of the Diffuse series. The intensities of the "4481" lines, however, are graded as in an ordinary series, and the chief objection to uniting them in a single formula in the first discussion was the undesirability of introducing a new type of series formula for what seemed to be a special case, so long as the older formulæ could be employed. This objection is no longer valid, because, as will appear later, several other series of the same type, occurring in associated groups, have since been recognised.

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* 'Handbuch der Spectroscopie,' Band II., p. 514.

From the formulæ previously given for the two divisions of the "4481" lines, it was evident that all the lines could be combined, at least very nearly, in one equation if desired. There were, however, small deviations, apparently systematic, which suggested that the union was not quite exact, but these have been removed by the new measurements, which became necessary when it appeared that the lines were doublets. It can no longer be doubted that the lines form a single series, differing from the more familiar series in that the lines occur twice as frequently; *i.e.*, if the ordinary formulæ involving the Rydberg constant N be employed, we find lines corresponding not only to the integral values m, but also to $m+\frac{1}{2}$. It will, however, be more convenient to employ formulæ in which m takes successive integral values only, N being then replaced by 4N or by a number of that order of magnitude.

As the positions of the lines have been determined with considerable precision, and the lines are fairly numerous, it seemed desirable to compare the accuracy of a variety of formulæ, some with N assumed the same as for hydrogen, and others with this term calculated from the lines themselves. The fact that not all the lines have been resolved, and the slight uncertainty as to the absolute positions of the last two or three lines of the series, renders the comparison to some extent wanting in finality, but the results may nevertheless be of interest.

For comparison of observed and calculated wave-numbers, the unresolved lines have been regarded as consisting of two components separated by 0·99, one having a wave-number greater by 0·33 than that of the unresolved line, and the other 0·66 less, since the more refrangible component is about double the intensity of the less refrangible. The wave-numbers adopted in the calculations for the less refrangible components, adjusted in this manner, are given in the first column of Table II. The wave-numbers are on the International scale, and have been corrected to vacuum. On this scale, the value of the Rydberg constant, according to an investigation by W. E. CURTIS* is 109,679·3.

* Not yet published.

The formulæ which have been calculated are as follows :—

I. Rydberg's, with N as for hydrogen,

$$n = 49{,}770{\cdot}45 - \frac{4\times 109{,}679{\cdot}3}{(m+0{\cdot}996943)^2} \qquad m = 3,\ 4,\ \ldots .$$

II. Rydberg's, with numerator calculated,

$$n = 49{,}781{\cdot}21 - \frac{4\times 109{,}883{\cdot}9}{(m+0{\cdot}999887)^2} \qquad m = 3,\ 4,\ \ldots .$$

III. Hicks', with N as for hydrogen,

$$n = 49{,}775{\cdot}20 - \frac{4\times 109{,}679{\cdot}3}{\left(m+0{\cdot}994541+\dfrac{0{\cdot}006170}{m}\right)^2} \qquad m = 3,\ 4,\ \ldots .$$

IV. Ritz's, with N as for hydrogen,

$$n = 49{,}774{\cdot}76 - \frac{4\times 109{,}679{\cdot}3}{\left(m-0{\cdot}004714+\dfrac{0{\cdot}021503}{m^2}\right)^2} \qquad m = 4,\ 5,\ \ldots .$$

V. Rydberg's, with numerator calculated, and $(m+\mu)$ assumed an integer

$$n = 49{,}781{\cdot}63 - \frac{4\times 109{,}891{\cdot}8}{m^2} \qquad m = 4,\ 5,\ \ldots .$$

VI. Same as V. ; least square solution, using all the lines,

$$n = 49{,}780{\cdot}44 - \frac{4\times 109{,}885{\cdot}65}{m^2} \qquad m = 4,\ 5,\ \ldots .$$

The observed *minus* computed values resulting from these formulæ are shown in Table II.

Table II.—Less Refrangible Components of Mg "4481" Series.

Wave-number (I.Å.), *in vacuo.*	Estimated limit of error.	I.	II.	III.	IV.	V.	VI.	Remarks.
22,308·68	0·02	0·00*	0·00*	0·00*	0·00*	0·00*	−0·35	
32,198·99	0·05	−1·30	0·00*	0·00*	0·00*	+0·05	+0·25	
37,571·43	0·14	0·00*	0·00*	0·00*	0·00*	0·00*	+0·51	
40,810·65	0·17	+1·43	−0·15	+0·21	+0·25	−0·22	+0·47	Lines unresolved but wave-numbers adjusted.
42,912·64	0·4	+2·39	−0·63	+0·25	+0·34	−0·75	+0·05	
44,353·99	1·0	+3·48	−0·71	+0·70	+0·85	−0·88	0·00	
45,384·70	1·0	+4·11	−1·05	+0·86	+1·06	−1·26	−0·31	
46,147·24	1·1	+4·57	−1·37	+1·00	+1·23	−1·60	−0·62	
(46,727·2)†				(+1·15)				

* Used in calculation of constants.

† Calculated from equation III. assuming estimated error of formula.

It will be seen that the lines are very closely represented by any of the formulæ. Even the simple Rydberg equation (I.) leaves no error so great as a quarter of an Ångström unit, and it would require wave-lengths of still greater accuracy to test the relative merits of the other formulæ. In each case, however, the residuals, although very small, are sufficiently systematic to indicate that not one of the formulæ can be considered exact, unless some unrecognised source of systematic error in the determination of the wave-numbers may eventually be traced. In choosing between the different forms of equation it is accordingly necessary to be guided by experience of their application to other series of the same character, if they can be found. The result of such trials, as will presently appear, is to indicate that the Hicks form of equation is the one which most closely accords with the observations in general.

In the absence of an exact formula, a consideration of the residuals given in Table II. indicates that the limits of the "4481" series may be taken as 49778·0 and 49779·0 with very small probable error, and these values will be adopted in the subsequent discussion.

§ 4. *The Doublet Series of Calcium, Strontium, and Barium.*

Other series of lines apparently similar in character to the "4481" series of Mg were found in LYMAN's observations of narrow doublets of Ca, Sr, and Ba in the Schumann region,[*] combined with SAUNDER's observations in the ordinary ultra-violet. While the investigation was in progress, however, a discussion of the available observations of these series was published by E. LORENSER,[†] who also found that the ordinary formulæ could not be applied to them. LORENSER has further established that these series stand in the relation of Fundamental (F), or "Bergmann," series to the systems of series comprising the well-known wider doublets in the spectra of these elements, of which the H and K lines of calcium may be quoted as a familiar example. In each case the separation of the narrow doublets of the F series is identical with that of the first member and its satellite in the Diffuse (D) series of the wider doublets; and the limits of the F are apparently identical with the variable parts of the expressions for these lines.

Omitting Ba, which presents some difficulties, though generally conforming, LORENSER's formulæ[‡] are as follows, the Sharp series being indicated by S :—

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[*] 'Astrophys. Jour.,' vol. 35, p. 341 (1912).

[†] 'Dissertation,' Tübingen (1913).

[‡] Formulæ of this type were first employed for the doublets of Ba by SAUNDERS ('Astrophys. Jour.,' vol. 32, p. 164, 1910). In a later paper SAUNDERS also indicated a connection between the limits of the wide and narrow doublets ('Physical Review,' Series 2, vol. 1, p. 332, 1913).

Calcium—

$$\text{Wide doublets} \quad \ldots\ldots \quad \begin{cases} \mathrm{D}\,(m) = \left.\begin{matrix}70{,}117\\70{,}340\end{matrix}\right\} - \dfrac{423{,}416}{(m-0{\cdot}69117)^2}, \\[2ex] \mathrm{S}\,(m) = \left.\begin{matrix}70{,}117\\70{,}340\end{matrix}\right\} - \dfrac{421{,}559}{(m+0{\cdot}617844)^2}. \end{cases}$$

$$\text{Narrow doublets} \quad \ldots\ldots \quad \mathrm{F}\,(m) = \left.\begin{matrix}81{,}820{\cdot}0\\81{,}880{\cdot}8\end{matrix}\right\} - \dfrac{430{,}959}{(m-0{\cdot}039796)^2}.$$

Strontium—

$$\text{Wide doublets} \quad \ldots\ldots \quad \begin{cases} \mathrm{D}\,(m) = \left.\begin{matrix}64{,}154\\64{,}954\end{matrix}\right\} - \dfrac{410{,}836}{(m-0{\cdot}59254)^2}, \\[2ex] \mathrm{S}\,(m) = \left.\begin{matrix}64{,}154\\64{,}954\end{matrix}\right\} - \dfrac{415{,}157}{(m+0{\cdot}684636)^2}. \end{cases}$$

$$\text{Narrow doublets} \quad \ldots\ldots \quad \mathrm{F}\,(m) = \left.\begin{matrix}73{,}833{\cdot}5\\74{,}113{\cdot}2\end{matrix}\right\} - \dfrac{430{,}554}{(m-0{\cdot}056189)^2}.$$

The numeration of the members is shown in Tables III. and IV. (Lor.=Lorenser; Fow.=Fowler).

The negative terms corresponding to $m = 3$ in the D series, and to $m = 1{\cdot}5$ in the S series (the latter giving the first P doublet), are given very erroneously by the formulæ, as is so often the case in the more familiar series. Nevertheless, Lorenser has fully established the connection of the F with the D series, through the usual relations, to which reference has already been made. There is sufficient evidence that the lines in question are to be regarded as enhanced lines, and, though Lorenser does not appear to have recognised this fact, his work proved that enhanced lines may form groups of related series which are generally similar to those occurring in arc spectra, but require modifications of the usual formulæ.

It will be observed that in Lorenser's formulæ the numerator is of the order of 4N as in those already found for the Mg "4481" series, and the question arises whether 4N may not be the universal constant for enhanced lines, as N is universal for series of lines produced under less violent excitation. The series are not long enough to give a very satisfactory comparison of the relative accuracy of different formulæ, but, so far as it goes, the evidence is distinctly in favour of the Hicks formula with 4N for the numerator. For the F series the formula may take the simpler Rydberg form with sufficient accuracy.

The formulæ for the above series are then as follows, the wave-numbers being on Rowland's scale to facilitate comparison with Lorenser's figures:—

Calcium—

$$\text{Wide doublets . . . } \begin{cases} \mathrm{D}(m) = \left.\begin{matrix} 70{,}289{\cdot}2 \\ 70{,}512{\cdot}2 \end{matrix}\right\} - \dfrac{4 \times 109{,}675}{\left(m + 0{\cdot}396204 - \dfrac{0{\cdot}106980}{m}\right)^2}, \\[2ex] \mathrm{S}(m) = \left.\begin{matrix} 70{,}289{\cdot}2 \\ 70{,}512{\cdot}2 \end{matrix}\right\} - \dfrac{4 \times 109{,}675}{\left(m + 0{\cdot}222264 - \dfrac{0{\cdot}143832}{m}\right)^2}. \end{cases}$$

$$\text{Narrow doublets . . } \quad \mathrm{F}(m) = \left.\begin{matrix} 81{,}948{\cdot}6 \\ 82{,}009{\cdot}4 \end{matrix}\right\} - \frac{4 \times 109{,}675}{(m - 0{\cdot}013703)^2}.$$

Strontium—

$$\text{Wide doublets . . . } \begin{cases} \mathrm{D}(m) = \left.\begin{matrix} 64{,}323{\cdot}3 \\ 65{,}123{\cdot}3 \end{matrix}\right\} - \dfrac{4 \times 109{,}675}{\left(m + 0{\cdot}611476 - \dfrac{0{\cdot}283578}{m}\right)^2}, \\[2ex] \mathrm{S}(m) = \left.\begin{matrix} 64{,}323{\cdot}3 \\ 65{,}123{\cdot}3 \end{matrix}\right\} - \dfrac{4 \times 109{,}675}{\left(m + 0{\cdot}344681 - \dfrac{0{\cdot}233220}{m}\right)^2}. \end{cases}$$

$$\text{Narrow doublets . . } \quad \mathrm{F}(m) = \left.\begin{matrix} 73{,}968{\cdot}3 \\ 74{,}248{\cdot}0 \end{matrix}\right\} - \frac{4 \times 109{,}675}{(m - 0{\cdot}028718)^2}.$$

The numeration of the members is shown in Tables III. and IV.

Details as to wave-lengths and wave-numbers of the lines involved, as quoted by LORENSER, are shown in Tables III. and IV., which also indicate the differences between the wave-lengths observed and those calculated from the two sets of equations.

An inspection of the tables will show that the observations are more closely represented in every case, and especially in the case of the negative terms, by the Hicks formula involving 4N than by the formula which has been employed by LORENSER. The superiority of the former is further shown in the greater accuracy with which it proves the identity of the limits of the F series with the variable parts of the expressions for the first line of the D series and its satellite. LORENSER has assumed this identity in determining the limits of the F series, thus—

$$\begin{aligned} \mathrm{Ca}: \; & 70{,}117 + 11{,}703{\cdot}0 = 81{,}820{\cdot}0 \\ & 70{,}117 + 11{,}763{\cdot}8 = 81{,}880{\cdot}8 \\[1ex] \mathrm{Sr}: \; & 64{,}154 + 9{,}679{\cdot}5 = 73{,}833{\cdot}5 \\ & 64{,}154 + 9{,}959{\cdot}2 = 74{,}113{\cdot}2 \end{aligned}$$

If, however, the formulæ for the F series be calculated entirely from the F lines themselves we get the equations

TABLE III.—Calcium Doublets.

Wide—Diffuse series.						Wide—Sharp series.						Narrow—Fundamental series.				
λ (ROWLAND).	*n*.	*m*.		O – C (Δλ).		λ (ROWLAND).	*n*.	*m*.		O – C (Δλ).		λ (ROWLAND.)‡	*n*.	*m*.	O – C (Δλ).	
		LOR.	FOW.	LOR.	FOW.			LOR.	FOW.	LOR.	FOW.				LOR.	FOW.
– 8498·35*	– 11,763·8	3	2													
– 8542·47	– 11,703·0			– 2195	– 1825	– 3933·83†	– 25,413·5	1·5	2	– 259·5	– 130	1840·2	54,341	4	0·0	0·0
– 8662·50	– 11,540·9					– 3968·63†	– 25,190·6					1838·0	54,406			
3181·4*	31,423·8	4	3													
3179·45	31,443·0			0·0	0·0	3737·08	26,751·4	2·5	3	0·0	0·0	1555·1	64,304	5	0·0	0·0
3158·98	31,646·8					3706·18	26,974·5					1553·5	64,370			
2113·01	47,311·2	5	4	0·0	0·0	2208·95	45,256·6	3·5	4	0·0	0·0	1434·3	69,720	6	– 0·65	– 0·27
2103·47	47,525·8					2198·03	45,481·4					1433·1	69,778			
1815·0	55,096	6	5	– 0·08	+ 0·24	1851·3	54,016	4·5	5	+ 0·2	+ 0·3	1370·6	72,960	7	– 0·70	0·0
1807·8	55,316					1843·8	54,236					1369·1	73,040			
1680·5	59,506	7	6	– 0·76	0·0	1698·9	58,861	5·5	6	– 0·2	+ 0·3					
1674·1	59,733					1692·4	59,087									

* Satellites.

† First doublet of Principal series.

‡ Wave-lengths *in vacuo*.

TABLE IV.—Strontium Doublets.

Wide—Diffuse series.						Wide—Sharp series.						Narrow—Fundamental series.				
λ (Row-land).	n.	m.		O − C (Δλ).		λ (Row-land).	n.	m.		O − C (Δλ).		λ (Row-land).‡	n.	m.	O − C (Δλ).	
		Lor.	Fow.	Lor.	Fow.			Lor.	Fow.	Lor.	Fow.				Lor.	Fow.
−10,038·3*	− 9,959·2	3	2	−5945	−2823											
−10,328·3	− 9,679·5					−4077·88†	−24,515·7	1·5	2	−300·5	− 81	2166·11	46,151·6	4	0·0	0·0
−10,915·0	− 9,159·2					−4215·66†	−23,715·7					2152·82	46,436·4			
3475·01*	28,768·8	4	3	0·0	0·0											
3464·58	28,855·4					4305·60	23,219·2	2·5	3	0·0	0·0	1778·8	56,217	5	0·0	0·0
3380·89	29,569·7					4161·95	24,020·6					1769·8	56,503			
2324·60*	43,005·2	5	4	0·0	0·0											
2322·47	43,044·6					2471·71	40,445·9	3·5	4	0·0	0·0	1620·7	61,702	6	−1·4	−0·96
2282·14	43,805·2					2423·67	41,247·4					1613·3	61,985			
1995·7	50,092	6	5	+1·30	+0·5	2053·3	48,687	4·5	5	+ 0·93	+0·7					
1965·2	50,869					2020·5	49,477									
1847·0	54,142	7	6	+0·06	0·0											
1820·0	54,945															

* Satellites.

† First doublet of Principal series.

‡ Wave-lengths *in vacuo*, except in case of first pair.

$$\text{Ca}: \ \text{F}(m) = \left.\begin{matrix}82{,}044{\cdot}8\\82{,}105{\cdot}6\end{matrix}\right\} - \frac{444{,}561}{(m+0{\cdot}00586)^2},$$

$$\text{Sr}: \ \text{F}(m) = \left.\begin{matrix}74{,}236{\cdot}6\\74{,}516{\cdot}3\end{matrix}\right\} - \frac{455{,}055{\cdot}1}{(m+0{\cdot}025265)^2}.$$

Thus, when LORENSER's formula is used throughout the discrepancies are

$$\text{Ca}: \ 82{,}044{\cdot}8-81{,}820{\cdot}0 = 224{\cdot}8$$

$$\text{Sr}: \ 74{,}236{\cdot}6-73{,}833{\cdot}5 = 403{\cdot}1$$

The Hicks 4N formula gives the variable parts of the expressions for the first D lines and their satellites as

$$\text{Ca}: \ 70{,}289{\cdot}2+11{,}703{\cdot}0 = 81{,}992{\cdot}2$$

$$70{,}289{\cdot}2+11{,}763{\cdot}8 = 82{,}053{\cdot}0$$

$$\text{Sr}: \ 64{,}323{\cdot}3+\ 9{,}679{\cdot}5 = 74{,}002{\cdot}8$$

$$64{,}323{\cdot}3+\ 9{,}959{\cdot}2 = 74{,}282{\cdot}5$$

Comparing these values with the limits calculated from the observed F lines by means of the formula with 4N, we have the discrepancies reduced to

$$\text{Ca}: \ 81{,}992{\cdot}2-81{,}949 \quad = 43{\cdot}2$$

$$\text{Sr}: \ 74{,}002{\cdot}8-73{,}968{\cdot}3 = 34{\cdot}5$$

The discussion of the available data for calcium and strontium, therefore, leads to the conclusion that series consisting of enhanced lines may be represented by the formula of HICKS if the ordinary numerator N be replaced by 4N. It is, of course, to be understood that the formula is subject to the same limitations as the one involving N as applied to ordinary series.

There is, however, one important difference between the enhanced line series of Ca, Sr, and Ba, and the ordinary arc series of these and other elements, namely, that in the case of enhanced lines the first observed member of the Diffuse series appears with a negative sign, while in the corresponding ordinary series it has a positive sign. In each case the limit of the F series and the separation of the doublets are nevertheless derived from this first member taken with proper sign. This is the " new relation " discovered by SAUNDERS in connection with the wide and narrow doublets of Ca, Sr, and Ba, namely, "The convergence wave-number of the complex pair series (D) *plus* the wave-number of the first term equals the convergence wave-number of the narrow pair series (F)."

The modified Hicks formula may accordingly be employed with confidence in searching for possible relationships of the " 4481 " series with other series of enhanced lines of magnesium.

§ 5. *The Doublet System of Magnesium.*

The spectrum of magnesium, as is well known, also contains doublets similar to those occurring in calcium, strontium, and barium. They do not appear in the flame spectrum; they occur in the arc and are certainly intensified in the spark, and are therefore to be regarded as enhanced lines of Class I. **Lorenser** has discussed these lines, but has not identified any associated Fundamental series such as were found for the other three elements. The lines in question are indicated in Table V.

Table V.—Magnesium Wide Doublets.

Diffuse series.				Sharp series.			
λ (Rowland).	n.	m.		λ (Rowland).	n.	m.	
		Lor.	Fow.			Lor.	Fow.
				–2795·63* –2802·80*	–35,759·9 –35,668·4	1·5	1
2798·07 2790·88	35,728·7 35,820·7	3	2	2936·61 2928·74	34,043·1 34,134·6	2·5	2
1737·8 1735·0	57,544 57,637	4	3	1753·6 1750·9	57,025 57,113	3·5	3

Unfortunately, the observed lines are so few that the equations of the two series can only be determined completely by utilising all the lines in the calculation of constants, the limit derived from the Sharp series being assumed for the Diffuse. **Lorenser's** formulæ with the numeration indicated in Table V. are

$$\mathrm{S}\,(m) = \left.\begin{matrix}84{,}893{\cdot}0\\ 84{,}984{\cdot}5\end{matrix}\right\} - \frac{413{,}202{\cdot}5}{(m+0{\cdot}35060)^2},$$

$$\mathrm{D}\,(m) = \left.\begin{matrix}84{,}893{\cdot}0\\ 84{,}984{\cdot}5\end{matrix}\right\} - \frac{423{,}376{\cdot}6}{(m+0{\cdot}065474)^2}.$$

The Hicks formulæ for these series, with the numeration shown under "Fow." in Table V., are

$$\mathrm{S}\,(m) = \left.\begin{matrix}85{,}479{\cdot}8\\ 85{,}571{\cdot}3\end{matrix}\right\} - \frac{4\times 109{,}675}{\left(m+0{\cdot}938644-\dfrac{0{\cdot}036421}{m}\right)^2},$$

$$\mathrm{D}\,(m) = \left.\begin{matrix}85{,}479{\cdot}8\\ 85{,}571{\cdot}3\end{matrix}\right\} - \frac{4\times 109{,}675}{\left(m+0{\cdot}949439-\dfrac{0{\cdot}040110}{m}\right)^2}.$$

---

* Also the first doublet of the Principal series.

These Mg doublets are analogous to the wider doublets of Ca, Sr, and Ba :—(1) They occur under precisely similar experimental conditions; (2) They show similar Zeeman effects (RUNGE and PASCHEN); (3) The separations of the components—Mg 91·5, Ca 223, Sr 801, and Ba 1691—are roughly proportional to the squares of the atomic weights; (4) The limits of the series follow a natural sequence, decreasing in the usual way as the atomic weight increases.

The analogy, however, is incomplete. In Ca, Sr, and Ba, the first negative terms of the D series, (given by $m = 2$ in the Hicks formula) correspond, as already mentioned, to observed lines (Tables III. and IV.) having satellite separations identical with those of the doublets in the associated F series; in these cases the satellite lies on the violet side of the more refrangible component of the D doublet, and not on the red side of the less refrangible component as in the positive terms of the same series. In Mg, on the other hand, the D pair given by $m = 2$ in the Hicks formula has a positive sign, and no lines have been observed near the position of the negative term (25,350 or about λ 3940) given by $m = 1$. An associated F series, by analogy, would be expected to have its limits near 110,830 (= 85,480+25,350), but there is no evidence of the existence of such a series.

The absence of a negative term in the observed D doublets of Mg suggests, as an alternative view, that the associated F series may be derived from the first line actually observed, namely λ 2798. In that case LORENSER's formula would give for the limit of the F series: 84,893·0−35,728·7 = 49,164·3, and the Hicks formula 85,479·8−35,728·7 = 49,751·1.

These figures at once suggest the limit 49,778 of the "4481" series; and the available data for the Wide doublets are, in fact, consistent with the assumption that the agreement is exact. It would seem then that the "4481" series may be a Fundamental series deriving its limits from the first positive line of the D series of Wide doublets. In that case the D line λ 2798 would be expected to have a satellite with the same separation as the lines of the "4481" series, namely, $\delta n = 0·99$. A special search for the satellite has been made in the photographs of the arc *in vacuo* taken in the fourth order of the grating, but it has not been directly observed. Indirect evidence of its possible existence, however, is afforded by careful measurements of the intervals of the Wide pairs. The new wave-lengths are given on the International Scale in Table VI. It will be seen that while the pairs of the P and S series are in close agreement, indicating a normal separation of 91·5, the interval of the D pair is not less, as would usually be the case if a satellite were present, but greater. This is confirmed by the recent measures of these lines by NACHEN.[*] The measurements thus suggest that there is a satellite on the *more* refrangible side of the chief line, the separation being comparable with that in the "4481" series if we assume that the tabulated λ 2797·989 refers to the chief line itself. Such a reversal of the usual position of the satellite, however, would accord

[*] 'Zeitsch. f. Wiss. Photog.,' 1913, XII., 2, p. 59.

with the fact that the more refrangible component of the "4481" lines is also the stronger.

While it is thus probable that the "4481" series is numerically related to the D series of Wide doublets, there are objections to regarding it as directly derived from that series—

(1) The "4481" lines, unlike the doublets, do not occur in the ordinary arc; (2) The separation of the components of the "4481" lines is much too small compared with the F doublets of Ca, Sr, and Ba; the latter are roughly proportional to the squares of the atomic weights—Ca 65, Sr 285, Ba 575—and a corresponding F series of Mg would be expected to have a separation of about 20 in place of the 0·99 actually observed in the "4481" lines.

The probable nature of the relation, however, has been revealed by the discovery of a new system of doublets, with which the "4481" series appears to be directly associated. Before referring to these new lines it will be convenient to give further data for the Wide doublets, for comparison with similar data which will appear later for the new series. On the assumption that the variable part of the expression for the first observed pair of the D series is identical with one limit of the "4481" series, the corrected limit of the less refrangible components (I.Å.) becomes 49,779·0+35,729·6, or 49,778·0+35,730·6* = 85,508·6, and that of the more refrangible components, 85,508·6+91·5 = 85,600·1. These values have been utilised in the construction of Table VI. It is only necessary to explain that the symbols *m*D, *m*S,

TABLE VI.—Mg Wide Doublets. Revised Data.

$$\text{Limits}\left\{\begin{array}{l}85{,}508\cdot6.\\85{,}600\cdot1.\end{array}\right.$$

m.	D series.				S series.			
	λ (I.Å.).	*n*.	δ*n*.	*m*D.	λ (I.Å.).	*n*.	δ*n*.	*m*S.
1					−2795·523†	−35,761·15	91·54	121,269·7
					−2802·698†	−35,669·61		121,269·7
2	2797·989	35,729·63 (35,730·6)‡	92·44	49,779·0 49,778·0	2936·496	34,044·44	91·48	51,464·2
	2790·768	35,822·07		49,778·0	2928·625	34,135·92		51,464·2
3		57,546 57,639		27,962·6 27,961·1		57,027 57,115		28,481·6 28,485·1

* Assumed wave-number of satellite to λ 2797·989.

† First P doublet.

‡ Wave-number of probable satellite.

in the convenient notation adopted by PASCHEN in his extensive researches on series, represent the differences between the wave-numbers of the observed lines and the limits of the series to which they belong. Thus, if the Hicks equation were exact, the symbol 3D would be an abbreviation for $4\mathrm{N}\Big/\left(m+\mathrm{D}+\frac{\Delta}{m}\right)^2$ when m has the value 3, and so on. Defects of formulæ are eliminated in evaluating the variable parts of the expressions in this manner, except as regards the determination of the limits. In the present case it is probable that the limits are also exact.

The differences between the two values of 3D, and between those of 3S are to be attributed to errors of observation.

§ 6. *A New System of Magnesium Doublets.*

Two conspicuous doublets, a little more refrangible than λ 4481 (Plate 3, fig. 2), were recorded in the magnesium arc *in vacuo* by FOWLER and PAYN in 1903.[*]

Following E. E. BROOKS,[†] who also investigated their occurrence in the magnesium spectrum, it will be convenient to designate these the "F and P" or "F.P." Doublets in order to distinguish them from the "Wide" Doublets which have already been discussed, and to avoid confusion with the term "Narrow" Doublets as applied to the F series of Ca, Sr, and Ba. The wave-lengths of these lines were given more accurately by FOWLER[‡] in a later paper as 4434·20, 4428·20, 4390·80, and 4384·86 (ROWLAND), from which the wave-number intervals in the two doublets are 30·5 and 30·8 respectively.

The lines evidently form two related pairs, and the experimental conditions for their production are identical in every respect with those for λ 4481, thus differing from the Wide Doublets in the ultra-violet. It appeared, therefore, that the "F.P." Doublets might belong to series, the investigation of which would throw further light on the relationships of the "4481" series.

Six other doublets with the same interval were eventually traced, and an additional one in the infra-red has been recorded by LORENSER. The doublets occur in groups of two, the more refrangible being slightly the stronger in each group. They fall readily into two series, and as in the other enhanced line series which have been considered, it is necessary to employ the term 4N for the numerator in the formulæ.

The stronger doublets have been regarded as belonging to the Diffuse, and the weaker ones to the Sharp series. According to HICKS this classification is supported by the signs of the last terms of the denominators when his formula is employed.

Measurements of the lines have been made on photographs taken with the quartz spectrograph (Plate 3, figs. 4 and 5), with the exception of the doublets near λ 4481,

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[*] 'Roy. Soc. Proc.,' 1903, vol. 72, p. 255.

[†] 'Roy. Soc. Proc.,' 1907, vol. 80, p. 220.

[‡] 'Phil. Trans.,' A, 1909, vol. 209, p. 451.

TABLE VII.—New ("F.P.") Doublets of Magnesium.

m.	Diffuse series.					Sharp series.				
	λ (ROWLAND).	λ (I.Å.).	n, *in vacuo* (I.Å.).	δn.	O – C, Δn.	λ (ROWLAND).	λ (I.Å.).	n, *in vacuo* (I.Å.).	δn.	O – C, Δn.
2		– 10897·8*	– 9,172·1*				– 9334·8*	– 10,709·8*		
		– 10934·2*	– 9,141·6*				– 9361·5*	– 10,679·3*		
3	7896·63†	7896·37	12,660·6	30·9	0·0‡		8227·5*	12,154·4*		
	7877·39†	7877·13	12,691·5				8206·9*	12,184·9*		
4	4390·751	4390·585	22,769·73	30·86	0·0‡	4434·159	4433·991	22,546·84	30·53	0·0‡
	4384·809	4384·643	22,800·59			4428·163	4427·995	22,577·37		
5	3539·00	3538·86	28,249·8	30·5	0·0	3553·65	3553·51	28,133·3	30·9	0·0
	3535·18	3535·04	28,280·3			3549·75	3549·61	28,164·2		
6	3169·11	3168·98	31,546·9	30·3	0·0‡	3175·97	3175·84	31,478·8	30·3	0·0‡
	3166·07	3165·94	31,577·2			3172·92	3172·79	31,509·1		
7	2967·98	2967·87	33,684·5	30·5	+1·8	2971·81	2971·70	33,641·1	30·4	+1·5
	2965·30	2965·19	33,715·0			2969·13	2969·02	33,671·5		

* Calculated only.

† Observed by LORENSER.

‡ Used in calculation of constants.

the wave-lengths of which have been redetermined from plates taken in the 3rd and 4th orders of the grating. International standards were employed in the determinations but the wave-lengths on both scales are given in Table VII.

For these "F.P." doublets the small letters d, s, and p will be used for the Diffuse, Sharp, and Principal series respectively, D, S, and P being reserved for the corresponding series of Wide doublets.

Employing the less refrangible components of the first, second, and fourth doublets for the calculation of constants, the resulting equation for the d series is

$$d\,(m) = \left.\begin{matrix} 40{,}618{\cdot}45 \\ 40{,}648{\cdot}95 \end{matrix}\right\} - \frac{4 \times 109{,}679{\cdot}3}{\left(m + 0{\cdot}947218 + \dfrac{0{\cdot}042317}{m}\right)^2}$$

and for the s series, assuming the same limits and calculating from the first and third of the less refrangible components

$$s\,(m) = \left.\begin{matrix} 40{,}618{\cdot}45 \\ 40{,}648{\cdot}95 \end{matrix}\right\} - \frac{4 \times 109{,}679{\cdot}3}{\left(m + 0{\cdot}930{,}683 - \dfrac{0{\cdot}014220}{m}\right)^2}.$$

These equations represent all the observations very closely as will be seen from the columns "O−C" in Table VII.

§ 7. *Relation between the* "4481" *and the New Series.*

A connection between the "F.P." doublets and the "4481" series is indicated by the above equation for the d series, since $m = 2$ gives the variable part as 49,790·5 which is very close to the limits of the "4481" series. By analogy with the doublets of Ca, Sr, and Ba, this would be the case if the "4481" series were a Fundamental series forming part of the "F.P." system. Such an association would conform with the rule already indicated by the other three elements that the limit of the Fundamental series in the case of enhanced lines is derived from the first negative term of the d series, and not from the first positive as in arc line series.

For the complete establishment of this relation the lines of the d series should be found to have satellites; and in the case of the first member the separation of the satellite should be equal to that of 4481. The wave-length of the first line is given by the Hicks formula as near λ 10,900, a position which does not fall within the region which could be observed with the instruments available. The satellite separation should be $\delta\lambda = 1{\cdot}2$. The second d pair (λ 7896), which should have a satellite separation $\delta\lambda = 0{\cdot}25$, is also outside the region investigated. At the third (λ 4390·6) the satellite separation would be reduced to $\delta\lambda = 0{\cdot}04$ ($\delta n = 0{\cdot}21$) which is too small for resolution. There is, however, some evidence of a disturbance of the position of the third line (Table VII.). This part of the spectrum was photographed in the 3rd and 4th orders of the grating, and careful measurements have shown that the λ 4390 *d* doublet is slightly wider (0·3) than the neighbouring doublet of the *s* series. Lorenser's interval for the second *d* pair is also greater than that of the other doublets which have been measured. The intervals of the remaining pairs have been less accurately determined and cannot be used for such a comparison. As in the case of the corresponding line λ 2798 of the Wide doublet (D) series, the observations of the λ 4390 doublet suggest a satellite on the *more* refrangible side of the chief line, and this unusual position would accord with the greater strength of the *more* refrangible components of the "4481" series.

The "4481" series may accordingly be considered to be associated with either of the two systems of doublets, but a more direct connection with the "F.P." group is indicated by the fact that these lines occur under precisely the same experimental conditions as 4481. With this relation no difficulty arises with regard to the small interval of the "4481" lines, or to the limits of the series when compared with the corresponding figures for Ca, Sr, and Ba. It may therefore be concluded that the "4481" series is the Fundamental series of the "F.P." system.

§ 8. *The Principal Series of the New Doublet System.*

Associated with the "F.P." doublets a Principal series would also be expected. The approximate formula for the more refrangible components of these doublets, calculated in the usual way from that of the *s* series, is

$$p(m) = 51{,}328{\cdot}2 - \frac{4 \times 109{,}679{\cdot}3}{(m+1{\cdot}286480)^2}.$$

This indicates the neighbourhood of λ 9340 for the first *p* doublet (which should have $\delta n = 30{\cdot}5$) and λ 3643 for the second. The first is outside the range of the present observations, but the second is probably represented by one of two similar pairs of lines which are developed under the same conditions as the "F.P." lines. In each pair the more refrangible component is the stronger, as it should be in the *p* series, and the separations are about that which would be expected in the second member. Particulars of these lines are as follows:—

λ (I.Å.).	*n*.	δ*n*.	Remarks.
3850·40	25,964·1	14·6	Probable "combination" doublet (Plate 3, fig. 8).
3848·24	25,978·7		
3615·64	27,650·0	14·0	Probable *p* doublet.
3613·80	27,664·0		

It is evident that both pairs cannot belong to the *p* series, and the near equality of the intervals therefore suggests that one belongs to the *p* series while the other is a "combination" doublet. We have, in fact, the following numerical relations with the term $2d$ given by the limit of the more refrangible (stronger) components of the "4481" series:—

$$49{,}779\cdot0-25{,}978\cdot7 = 23{,}800\cdot3,$$

$$49{,}779\cdot0-25{,}964\cdot1 = 23{,}814\cdot9.$$

$$\left.\begin{array}{l} 23{,}800\cdot3+27{,}664\cdot0 = 51{,}464\cdot3 \\ 23{,}814\cdot9+27{,}650\cdot0 = 51{,}464\cdot9 \end{array}\right\} \text{mean } 51{,}464\cdot6.$$

The last number is not far from the approximate limit calculated for the *p* series, and it is suggested that the lines at λ 3615 form the *p* doublet while the other pair is a combination derived from this and the limit of the "4481" series ($f\,\infty-3p$, or $2d-3p$).

A striking confirmation of this conclusion is afforded by the fact that the term 2S for the Wide doublet series (Table VI.) is 51,464·2. This is not only in close accordance with the limit for *p* calculated above, but is an important indication of the intimate connection of the two systems of doublets. It will suffice for the present to note that the limit of the *p* series of "F.P." doublets appears to be given by the difference between the limit of the subordinate Wide doublets and the wave-number of the first observed S line which has a *positive* value; or, symbolically, $p\,\infty = 2\text{S} = \text{S}\,\infty-\text{S}\,(2)$.

The agreement is too close to be regarded as accidental, and assuming the relation to be true, the limit of the *p* series can be determined very exactly. The limit of the "4481" series (giving 2D and thence S ∞) has been found with considerable precision and the wave-number of the line λ 2936·496 giving S (2), has also been accurately determined. Hence, with very small probable error, the limit of the *p* series may be taken as 51,464·2. The limits of the *d* and *s* series (40,618·4 and 40,648·9) are probably also not far from the truth, and the wave-numbers of the components of the *first p* pair may therefore be deduced by the Rydberg-Schuster law. Hence, although only the second *p* doublet has been actually observed, there are sufficient data for the calculation of Hicks' formulæ for the series, namely,

$$p_2\,(m) = 51{,}464\cdot2-\frac{4\times109{,}679\cdot3}{\left(m+1\cdot305940-\dfrac{0\cdot041388}{m}\right)^2},$$

$$p_1\,(m) = 51{,}464\cdot2-\frac{4\times109{,}679\cdot3}{\left(m+1\cdot307258-\dfrac{0\cdot041556}{m}\right)^2}.$$

The positions of the first four doublets calculated from these equations are as follows:—

TABLE VIII.—Principal Series of " F.P." Doublets.

Limit = 51,464·2.

m.	λ (I.A.).	*n*.	mp_2. mp_1.	δ*n*.	Remarks.
2	9243·7	10,815·3	40,648·9	30·5	Calculated.
	9217·7	10,845·8	40,618·4		
3	3615·64	27,650·0	23,814·2	14·0	Observed.
	3613·80	27,664·0	23,800·2		
4	2790·84	35,819·9	15,644·3	7·6	Calculated.
	2790·35	35,827·5	15,636·7		
5	2474·37	40,402·4	11,061·8	4·5	
	2474·09	40,406·9	11,057·3		

The Principal series thus appears to be satisfactorily identified, but it is somewhat remarkable that it does not occur with greater intensity.

§ 9. *Relation between the Two Systems of Doublets.*

The connection of 4481 with the Wide doublets appears to arise from the fact that the two sets of doublets are themselves closely related. An indication of this has already been noted in connection with the limit of the *p* series. Further evidence is afforded by a comparison of other terms of the two systems. Thus, for the Wide doublets, including the case just mentioned, we have from Table VI.,

$$S_1\infty = 85{,}508{\cdot}6,$$

$$S_2\infty = 85{,}600{\cdot}1,$$

$$2D = 49{,}778{\cdot}0, \qquad 2S = 51{,}464{\cdot}2,$$

$$3D = 27{,}961{\cdot}8, \qquad 3S = 28{,}483{\cdot}3,$$

all of which are derived from actual observations, and are, therefore, unaffected by any imperfections of formulæ except as regards the limits of the " 4481 " series. The equations for the *d*, *s*, and *p* series of " F.P." doublets (pp. 244 and 246) give corresponding terms,

$$1p_1 = 85{,}462{\cdot}9,$$
$$1p_2 = 85{,}550{\cdot}2.$$
$$2d = 49{,}790, \qquad 2s = 51{,}328,$$
$$3d = 27{,}958, \qquad 3s = 28{,}464.$$

The calculated terms of the "F.P." doublets may thus be considered identical with the corresponding terms of the Wide doublets, within the possible limits of error. In that case the corresponding subordinate series would run parallel to each other in the two systems at distance apart of

$$S_1\infty - s_1\infty = 85{,}508{\cdot}6 - 40{,}618{\cdot}4 = 44{,}890{\cdot}2 = P_1(2) - P_1(1)$$

and

$$S_2\infty - s_2\infty = 85{,}600{\cdot}1 - 40{,}648{\cdot}9 = 44{,}951{\cdot}2 = P_2(2) - P_2(1).$$

A further important indication of a close connection between the two systems results from a consideration of the P series of Wide doublets, of which only the pair λλ 2802, 2795 falls within the region of observation. In view of the relations of the other series to which reference has been made, the limit of the P series is probably given exactly as $85{,}508{\cdot}6 + 35{,}761{\cdot}1$, or $85{,}600{\cdot}1 + 35{,}669{\cdot}6 = 121{,}269{\cdot}7$ as shown in Table VI. With this limit, the formulæ for the two components of the series, derived from the observed pair are,

$$P_2(m) = 121{,}269{\cdot}7 - \frac{4 \times 109{,}679{\cdot}3}{(m + 1{\cdot}263889)^2},$$

$$P_1(m) = 121{,}269{\cdot}7 - \frac{4 \times 109{,}679{\cdot}3}{(m + 1{\cdot}265100)^2}.$$

From these equations we find for the P series the results shown in Table IX.

TABLE IX.—Principal Series of Wide Doublets (Preliminary Calculation).

Limit = 121,269·7.

m.	λ (I.Å.).	*n*.	*m*P₂. *m*P₁.	δ*n*.	Remarks.
1	2802·698	35,669·6	85,600·1	91·5	Observed lines (Table VI.).
	2795·523	35,761·1	85,508·6		
2	1248·64	80,087·1	41,182·6	30·5	Calculated.
	1248·16	80,117·6	41,152·1		
3	1029·45	97,138·8	24,130·9	13·7	
	1029·31	97,152·5	24,117·2		

The first striking result derived from these calculations is that the separation of the second member is 30·5, which is exactly that of the *d* and *s* doublets of the "F.P." system. Hence it is suggested that the variable parts $m\mathrm{P}_1$, $m\mathrm{P}_2$ are really identical with corresponding terms of the *p* series (Table VIII.). The differences are in fact not too great to be attributed to defects of the simple formulæ employed. Thus the P and *p* series may also be considered as running parallel to each other at a distance apart of $\mathrm{P}\infty - p\infty = 121{,}269{\cdot}7 - 51{,}464{\cdot}2 = 69{,}805{\cdot}5 = \mathrm{S}(2) - \mathrm{S}(1)$. Since the data for the *p* series depend upon more complete observational material than those for P, the latter may be corrected by the former, with the following results:—

Table X.—Corrected Principal Series of Wide Doublets.

Limit = 121,269·7.

m.	λ (I.Å.).	*n*.	$m\mathrm{P}_2$. $m\mathrm{P}_1$.	δ*n*.	Remarks.
1	2802·698	35,669·6	85,600·1	91·5	Observed lines (Table VI.).
	2795·523	35,761·1	85,508·6		
2	1240·37	80,620·8	40,648·9	30·5	Calculated.
	1239·90	80,651·3	40,618·4		
3	1026·11	97,455·5	23,814·2	14·0	
	1025·96	97,469·5	23,800·2		

Even the second pair is beyond the region photographed by Lyman in the case of magnesium, but it is not outside the limit of possible observation.

The foregoing considerations leave no doubt that while the limits and separations of the D and S series of Wide doublets are derived in the usual manner from the first doublet of the P series, those of the *d* and *s* series of the narrower "F.P." doublets are derived from the *second* P pair (Wide doublets). Paschen's work on Combination series appears to justify the belief that the Rydberg-Schuster law of limits, and Runge's law as to the derivation of the limit of the Fundamental series from the first line of the Diffuse series, are both exact, and the parallelism of the two systems thus permits the accurate calculation of data for both, since data lacking in one may be adopted from the other. For example, the term 2*s* of the "F.P." group is given by calculation as 51,328·2, and 1*s* as 119,449·3; both may be obtained with a much higher degree of precision by adopting the values 2S and 1S of the Wide doublet system (Table VI.), which are themselves independent of formulæ except as regards the determination of the limits of the "4481" series. The following table (XI.) may

TABLE XI.—The "F.P." Doublet System of Magnesium (Wave-numbers and "Variable Parts").

m.	*d* series.		*s* series.		*f* ("4481") series.		*p* series.	
	Limits {40,618·4. 40,648·9.		Limits {40,618·4. 40,648·9.		Limits {49,778·0. 49,779·0.		Limit, 51,464·2.	
	n.	*md*.	*n*.	*ms*.	*n*.	*mf*.	*n*.	mp_2. mp_1.
1		(110,836)		121,269·7*		(109,576·1)†	−34,135·9‡ −34,044·4‡	85,600·1 85,508·6
2		49,779·0		51,464·2*		(48,823·6)†		40,648·9 40,618·4
3	12,660·6 12,691·5	27,957·8		28,483·3*	22,308·7 22,309·7	27,469·3	27,650·0 27,664·0	23,814·2 23,800·2
4	22,769·7 22,800·6	17,848·7	22,546·8 22,577·4	18,071·6	32,199·0 32,199·9	17,579·0		15,644·3 15,636·7
5	28,249·8 28,280·3	12,368·6	28,133·3 28,164·2	12,485·1	37,571·4 37,572·4	12,206·6		11,061·8 11,057·3
6	31,546·9 31,577·2	9,071·5	31,478·8 31,509·1	9,139·6	40,811·3	8,967·4		
7	33,684·5 33,715·0	6,933·9	33,641·1 33,671·5	6,977·3	42,913·3	6,865·4		
8		(5,473·9)		(5,502·9)	44,354·7	5,424·0		
9					45,385·4	4,393·3		
10					46,147·9	3,630·8		
11						(3,050·8)†		

* From Table VI. (mS); $1s = \mathrm{P}\infty$.

† From HICKS' formula for "4481" series (equation III., p. 232).

‡ Observed S doublet (Table VI.), S (2); the variable parts in this case are $1\mathrm{P}_2$ and $1\mathrm{P}_1 = \mathrm{S}_2\infty$ and $\mathrm{S}_1\infty$.

accordingly be drawn up for the "F.P." system, it being understood that the variable parts of the *p*, *d*, and *s* series are equally applicable to the Wide doublets. In each case the terms *md*, &c., are given as derived from the observed wave-number of the less refrangible components; they would be the same for the more refrangible components if there were no errors of observation. The wave-numbers included are those which have been actually observed; others may readily be obtained from the limits and variable parts given. Terms depending wholly on calculation from formulæ are enclosed in brackets, and for simplicity the satellite has been disregarded. Further reference to this table will be made in the discussion of Combination series.

§ 10. *Combination Lines and Series of Magnesium.*

In the discussion of series, the wave-number of a line is represented by the difference of two other wave-numbers, the first of which (the limit) is constant for a given series, and the other variable, the limit itself appearing as one of the variable parts in an associated series. Combination lines and series, as is well known from the work of RITZ and PASCHEN, are formed by taking differences between the variable parts from different series. The Fundamental series was regarded by RITZ as a special type of Combination series, in which the variable part, in a doublet series, is given by $m\,(p_1 - p_2)$, or $m\,\Delta p$, where p_1 and p_2 are taken from the formulæ for the two components of the Principal series, or derived from the constant separation in the Diffuse and Sharp series. This relation, however, is only approximate, and *mf* will be used to denote the variable part in the Fundamental series. It should be recalled that if there are no satellites in the D series, the F series consists of single lines, and that when satellites are present in a doublet system, the F lines are also doublets, with a separation equal to that of the satellite and chief line in the first member of the D series.

The whole of the "F.P." system may be considered to consist of Combination series derived from the Wide doublets, or *vice versâ*. Retaining the use of capital letters for the Wide, and small ones for the "F.P." doublets, and disregarding the satellites, we have the relations

$$p_2(m) = 2\mathrm{S} - m\mathrm{P}_2, \qquad \mathrm{P}_2(m) = 1s - mp_2,$$
$$p_1(m) = 2\mathrm{S} - m\mathrm{P}_1. \qquad \mathrm{P}_1(m) = 1s - mp_1.$$

$$s_1(m) = 2\mathrm{P}_1 - m\mathrm{S}, \qquad \mathrm{S}_1(m) = 1p_1 - ms,$$
$$s_2(m) = 2\mathrm{P}_2 - m\mathrm{S}. \qquad \mathrm{S}_2(m) = 1p_2 - ms.$$

$$d_1(m) = 2\mathrm{P}_1 - m\mathrm{D}, \qquad \mathrm{D}_1(m) = 1p_1 - md,$$
$$d_2(m) = 2\mathrm{P}_2 - m\mathrm{D}. \qquad \mathrm{D}_2(m) = 1p_2 - md.$$

$$f(m) = 2\mathrm{D} - mf \quad \text{or} \quad 2\mathrm{D} - m(\mathrm{P}_1 - \mathrm{P}_2).$$

Either of the groups might be approximately determined in this way from the other, but an accurate knowledge of all the data for one of them can only be obtained by utilizing observations of both.

An interesting extension of the investigation of magnesium has been made possible by the production of a number of new lines of moderate intensity, which occur under the same experimental conditions as the "F.P." group (Plate 3, figs. 1, 2, 3). For some time the appearance of these lines seemed rather capricious, and it was thought that they might possibly be due to impurities. It was eventually found, however, that they could always be obtained in a small region near the negative pole of the arc *in vacuo*, provided a sufficiently heavy current (7 or 8 amperes) were employed. The lines were shown clearly in many photographs, where the only lines traceable to impurities were faint ones of Na, Ca, and Ba. No further doubt can be felt as to the magnesium origin of the lines, in view of the manner in which their positions can be calculated from the constants for the doublets, taken from Table XI.

One of the combination terms has already been utilised in the discussion of the p series. This is represented by the combination $2d-3p_1$, $2d-3p_2$, giving the lines λλ 3850·40, 3848·24, which form a well-marked doublet, shown very clearly in Plate 3, fig. 8.

In addition, two well defined Combination series have been identified. A few of the lines involved appear in a list given by Lorenser, but their connections were not then recognised. One of these series is somewhat stronger than the other and may be distinguished as Series A, the weaker being designated Series B. In each case the intensities degrade in the usual way in passing to the violet (Plate 3, figs. 1, 2, 3). Series A results from the combination $3d-mf$, and B from $3f-mf$. Details of the observations and comparisons with the calculations are given in Tables XII. and XIII.

Table XII.—Magnesium Combination Series A ($3d-mf$).

Limit, $3d$ = 27,957·8.

m.	λ (I.Å.) (Fowler).	n (observed).	n (calculated).	O – C, Δn.	Remarks.
5	6346·67	15,752·0	15,751·2	+0·8	Lor. gives λ 6347·27 (Row.).
6	5264·14	18,991·3	18,990·4	+0·9	,, ,, λ 5264·2 ,,
7	4739·59	21,093·1	21,092·4	+0·7	
8	4436·48	22,534·2	22,533·8	+0·4	
9	4242·47	23,564·7	23,564·5	+0·2	,, ,, λ 4242·60 ,, Mg?
10	4109·54	24,326·9	24,327·0	–0·1	
11	4013·80	24,907·1	24,907·0	+0·1	

TABLE XIII.—Magnesium Combination Series B ($3f-mf$).

Limit, $3f = 27{,}469{\cdot}3$.

m.	λ (I.Å.) (FOWLER).	n (observed).	n (calculated).	O − C, Δn.	Remarks.
5	6545·80	15,272·8	15,262·7	+10·1	LOR. gives { λ 6546·77 (Row.). λ 6545·66 ,,
6	5401·05	18,509·9	18,501·9	+ 8·0	,, ,, λ 5401·2 ,,
7	4851·10	20,608·2	20,603·9	+ 4·3	
8	4534·26	22,048·2	22,045·3	+ 2·9	
9	4331·93	23,078·1	23,076·0	+ 2·1	
10	4193·44	23,840·2	23,838·5	+ 1·7	
11	4093·90	24,419·8	24,418·5	+ 1·3	

It will be observed that in each case there is a systematic difference between observation and calculation. In Series A, however, the differences are very slight, and possibly negligible; but in Series B they are too large to be attributed to faulty observations. The terms mf have been derived from observations of a high order of accuracy, and in the case of Series B, the calculated wave-numbers would not be affected by any error in the adopted value of the limit of the f series. It is scarcely probable that Series B, with its limit so near to $3f$, is independent of the "F.P." system, and it would therefore appear that the combination principle is not exact in every case, except probably as regards the values of the limits.

Calculations of formulæ for the two series from the observed lines themselves confirm the values of the limits given by the combination terms. These formulæ are as follows:—

$$A\,(m) = 27{,}956{\cdot}48 - \frac{4 \times 109679{\cdot}3}{\left(m + 0{\cdot}993807 + \dfrac{0{\cdot}008967}{m}\right)^2},$$

$$B\,(m) = 27{,}468{\cdot}38 - \frac{4 \times 109679{\cdot}3}{\left(m + 0{\cdot}994863 + \dfrac{0{\cdot}014621}{m}\right)^2}.$$

The residuals (O−C) left by the formulæ on the observed wave-numbers are—

	$m =$ 5	6	7	8	9	10	11
O−C { Series A =	0·0*	+0·3	0·0*	+0·1	0·0	−0·3	0·0*
,, B =	0·0*	+1·8	0·0*	+0·1	0·0	0·0	0·0*

A general view of the enhanced line series of magnesium now identified is given in fig. 1, in which the doublet separations have been arbitrarily increased for greater clearness.

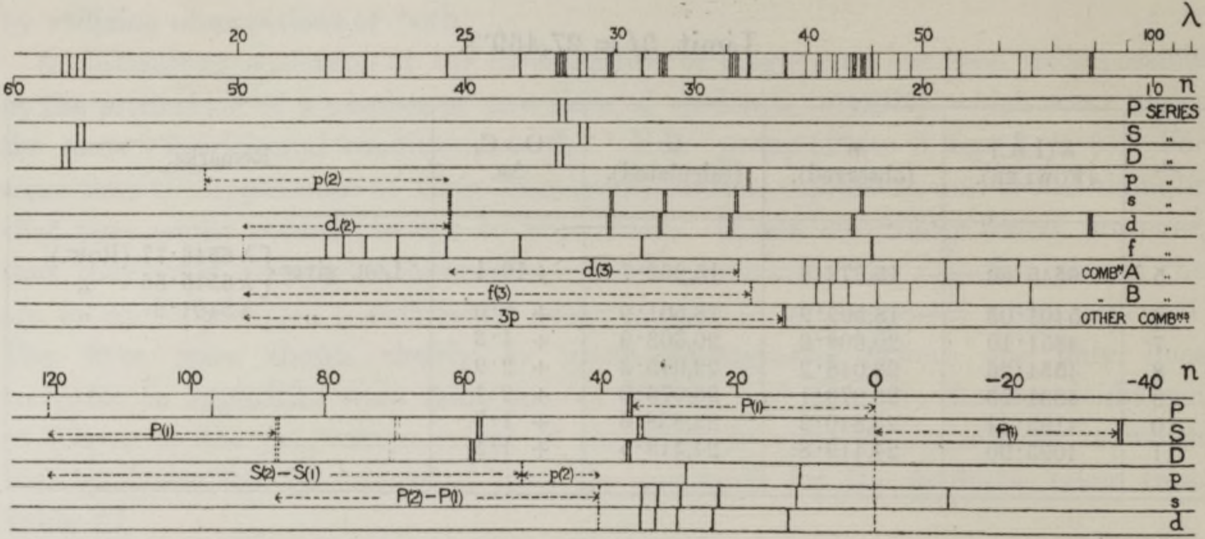

Fig. 1. Enhanced-line series of magnesium.

§ 11. *General Comparison of* Mg, Ca, Sr, *and* Ba.

One of the results of the investigation is to indicate that Mg behaves differently from Ca, Sr, and Ba in the spark. All are alike in having series of Wide doublets with separations related to the atomic weights, but the D doublet with negative frequency which occurs in the other three elements is lacking in Mg. While Ca, Sr, and Ba have strong Fundamental series with limits derived from the negative D doublet, the corresponding F series of Mg, like the negative term from which it should be derived, does not appear to exist. In Mg the equivalent of the F series of the other three elements is replaced by the whole system of "F.P." doublets (including the "4481" series as Fundamental), which has no analogue in the other three elements so far as is known at present. The "F.P." system itself is closely related to the family of Wide doublets, but although both consist of enhanced lines they do not necessarily co-exist; the wider system occurring in the ordinary arc, while the closer requires the conditions of the spark or its equivalent, the negative pole of an arc *in vacuo*.

The "4481" series is therefore established as a Fundamental series, but the system of which it forms a part is in some respects exceptional.

It is important to observe that no numerical relations between the enhanced and arc line series occurring in the spectra of any of the four elements have been recognised.

§ 12. *The Spectra of Hydrogen and Helium.*

The now demonstrated existence of series having 4N for the "universal" constant has an interesting bearing on the question of the origin of the special lines produced by strong discharges in helium tubes, to which reference has already been made. Some of these were at first regarded as being identical with the lines of the supposed P series of hydrogen calculated by RYDBERG on the assumption that the Pickering (ζ Puppis) lines formed the S series. The lines in question are compared with RYDBERG's values (Rowland scale) in the appended table :—

TABLE XIV.—The "4686" Series.

Observed λ (FOWLER).	Calculated λ (RYDBERG).	Difference Δλ.
4685·98	4687·88	1·90
3203·30		
2733·34	2734·55	1·21
2511·31		
2385·47	2386·50	1·03
2306·20		
2252·88	2253·74	0·86

In order to conform with RYDBERG's theory, and to adapt the formulæ then ordinarily employed, it was necessary, as in the first discussion of the Mg "4481" series, to divide the series into two parts by taking alternate lines. One series, as will be seen from the table, then agreed very closely with the calculated values for the P series of hydrogen, and the other was regarded as a second P series having a simple relation to the first.

The conditions of appearance of these lines in helium tubes indicates that they are enhanced lines, and calculation shows that they can be united in a single series of the 4N type, as in the case of the other series of lines of this class which have been discussed. Thus, the first line, which has been most accurately measured, gives the equation

$$n = 438{,}879{\cdot}1\left(\frac{1}{3^2}-\frac{1}{m^2}\right).$$

The differences O−C (Δn) for the seven observed lines are 0·0, −0·3, +1·4, +0·6, +1·0, +2·3, −1·4. All are within the estimated limits of error of observation, or very nearly so, except the third, and even in this case a correction of 0·1 Å.U. to the observed wave-length would reduce the difference to zero.

The "4686" series is accordingly a series of the enhanced line, or 4N, type, and can no longer be considered to belong to the same group as the Balmer series of hydrogen which is of the arc, or N, type. The numerical relations indicated by RYDBERG's calculations are therefore not significant, and, in view of the experimental evidence, it must be concluded that the "4686" series is not due to hydrogen, but to helium, as first indicated by Dr. BOHR from theoretical considerations. This conclusion is further supported by EVANS's observation of the line 4686 in a helium tube in which the ordinary lines of hydrogen could not be detected.* In accordance with the convenient nomenclature of LOCKYER it is suggested that the lines in question should be designated "proto-helium" lines.

Analogy with the magnesium "4481" series suggests that the "4686" series should be regarded as one of the F type, and the question arises as to how the associated P, S, and D series are represented in the proto-helium spectrum. A knowledge of the F series alone does not permit the complete calculation of any of the three associated series, but only indicates the "variable part" of the first line of the D series. In the case of proto-helium, the limit of the "4686" series, $N'/3^2$, shows that the variable part of the D formula is identical with that of the F, but the limit of D remains undetermined. A consistent arrangement is possible, however, if the D be regarded as having the same limit as the F series, in which case the four series would coalesce in the formula

$$n = N'\left(\frac{1}{3^2}-\frac{1}{m^2}\right)$$

where $N' = 438,879{\cdot}1$. This only requires that the zero values of n given by $m = 3$ be regarded as negative terms, so that if the formula be taken to represent the coalesced D and S series, the limit of P derived from S, and that of F derived from D would also be $N'/3^2$. The lines of the four series would thus be coincident. The great strength of the "4481" series of magnesium as compared with that of the other series of the "F.P." group, however, suggests that the "4686" series is primarily of the F type.

As pointed out by BOHR, the substitution of 4 for 3 in the above formula for the "4686" series yields a series of lines of which the Pickering (ζ Puppis) lines, also formerly attributed to hydrogen, are alternate members, the remainder being nearly coincident with the Balmer lines of hydrogen. It is probable, therefore, that the Pickering lines are also due to proto-helium, as they have only been observed in association with 4686. The calculated wave-lengths of the earlier members of the extended series are compared in Table XV. with the Balmer series, and with the hypothetical "sharp" series of hydrogen calculated by RYDBERG.

TABLE XV.—The "Pickering" Series.

Proto-helium, "Pickering" series, λ (calculated).	Hydrogen, Balmer series, λ.	"Hydrogen," RYDBERG'S S series, λ (calculated).
6560·37	6563·07	
5411·74		5412·8
4859·53	4861·52	
4541·79		4543·3
4338·86	4340·64	
4200·02		4201·5

---

* 'Nature,' 1913, September 4, p. 5.

The astrophysical and experimental data have as yet given no proof of the existence of the lines adjacent to those of hydrogen, but there is no evidence against the supposition that they exist.

The assignment of these lines to proto-helium is supported by the observations of magnesium, which have shown analogous series associated with the "4481" series. The series A of magnesium, given by the combination $3d-mf$, would become $4D-mF$ in proto-helium—the numeration being slightly different in the two cases*—and this would be identical with the formula for the extended Pickering series. Series B of magnesium, given by $3f-mf$, would similarly become $4F-mF$ and would also coalesce into the Pickering series. Alternate lines of series B are in fact not far removed from the Balmer lines, while intermediate lines are near the observed Pickering lines, as will be seen by comparing Tables XIII. and XV.; lines near these positions might also be derived from the F series of other elements in which mF approximates to $4N/m^2$. The relative weakness of the Pickering series of proto-helium, as compared with 4686, is matched in magnesium by the relatively low intensities of the analogous combination series A and B.

The close relations between the lines of hydrogen (real and hypothetical) and some of those of proto-helium are simply accounted for by BOHR's theory of the origin of these spectra. The general formulæ, in which p and m can only take integral values, may be written

$$\text{Hydrogen:} \quad n = \mathrm{N}\left(\frac{1}{p^2}-\frac{1}{m^2}\right) \qquad p = 2 \text{ for Balmer series.}$$

$$\text{Proto-helium:} \quad n = \mathrm{N}'\left(\frac{1}{p^2}-\frac{1}{m^2}\right) \qquad \begin{cases} p = 3 \text{ for ``4686'' series,} \\ p = 4 \text{ for Pickering series.} \end{cases}$$

If N′ were exactly equal to 4N, alternate lines of the Pickering series would evidently coincide with the Balmer series; and the hypothetical P series of hydrogen, given by $p = 1{\cdot}5$ in the first formula, would fall on alternate lines of the "4686" series.

The hydrogen lines, according to the theory, are produced during the binding of an electron by an atomic nucleus having a single positive charge, and those of proto-helium during the binding of an electron by a nucleus having four times the mass and a double positive charge. If the mass of the electron were negligible in comparison with that of the nucleus, N′ would be equal to 4N, but BOHR has shown that when correction is made for the mass of the electron, the theoretical ratio for these constants is in nearly perfect agreement with that of the values deduced from the spectroscopic observations.† His expression for the constant of the hydrogen series may be written

$$\mathrm{N}_{\mathrm{H}} = 109{,}675 \equiv \frac{10^8 2\pi^2 \mathrm{E}^2 e^2 \mathrm{M}m}{ch^3(\mathrm{M}+m)}$$

---

* The numeration would be the same if m in the proto-helium formula were written $(m+1)$ to correspond with $(m+0{\cdot}99)$ of magnesium.

† 'Nature,' 1913, October 23, p. 231.

where c is the velocity of light, h is PLANCK'S constant, e and m the charge and mass of the electron, and E and M the charge and mass of the nucleus of the hydrogen atom. In the case of proto-helium, the value of E is doubled and M is increased four times. The theoretical ratio between N′ and N is therefore

$$\frac{N_{pHe}}{N_{H}}=\frac{16(M+m)}{4(M+m)}.$$

Introducing the recognised value $M/m = 1835$, the resulting ratio is 4·001635, as compared with 4·001632 derived from the observations.

A spectroscopic method of determining the mass of the electron, from the constants of the hydrogen and proto-helium series, is thus suggested. The value of N′ obtained from λ 4685·98 ± 0·01 (ROWLAND'S scale) is 438,879·1 ± 1·0, and combining this with hydrogen 109,675, the resulting value for the mass of the hydrogen atom in terms of that of the electron is 1836 ± 12. A similar calculation from wave-lengths on the International scale, using Mr. CURTIS'S new value of the hydrogen constant (109,679·3) gives the ratio $M/m = 1855 \pm 12$. This result, however, is only to be regarded as provisional; more exact measures of the proto-helium lines may be possible, and the formula employed may require a small correction for the alteration in the mass of the electron due to its velocity.

The assignment of the "4686" series to proto-helium may nevertheless be considered to be independent of BOHR'S theory. It really depends upon the recognition of the new class of series associated with enhanced lines, and the better accordance with experimental results. Apart from the theory it might still be considered possible that the hydrogen spectrum, under appropriate conditions, would include the Rydberg lines. The well-known line about λ 4686 which occurs in the solar chromosphere and, in some of the nebulæ, however, is undoubtedly the proto-helium line, and there are no indications in these spectra of another line near 4688 which would correspond with the hypothetical line of hydrogen. Until other evidence is forthcoming, it may therefore be considered that the line spectrum of hydrogen, as required by BOHR'S theory, consists only of the Balmer series and parallel series in the infra-red and Schumann regions. These are all included in the simple formula previously given.

The proto-helium spectrum is apparently of the same simple character as that of hydrogen, but the series in the infra-red and Schumann regions have not yet been investigated.

§ 13. *Enhanced Lines in Relation to* BOHR'S *Theory.*

The apparently successful application of BOHR'S theory to the lines of proto-helium renders it desirable to consider briefly the implications of this theory as regards other systems of enhanced lines.

Since enhanced lines have been found to occur in families of series similar to those previously recognised in arc spectra, the only new theoretical problem presented by them is to account for the appearance of the series constant with four times the value associated with arc lines. Otherwise, the extension of the simple formulæ for proto-helium to enhanced lines in general is identical with the extension of BALMER'S formulæ for hydrogen to the ordinary systems of series of arc lines. Hydrogen and proto-helium may thus be regarded as limiting cases of the two kinds of series.

Independently of the series evidence there are numerous indications that enhanced lines originate in vibrating systems differing from those which give rise to arc lines. The mode of occurrence of the two sets of lines in the spectra of celestial bodies furnishes important evidence in favour of this view, and experimental evidence in the same direction is abundant. The extensive researches of HEMSALECH on the phenomena of the spark discharge, for example, have revealed striking differences in the behaviour of the two classes of lines.*

It has been shown that in a single discharge, the durations of the enhanced lines of Ca, Sr, and Mg, are much shorter with respect to their intensities than those of the arc lines of the same elements; and in another investigation it was shown that the velocities of the particles emitting the enhanced lines of Ca were nearly twice as great as those of the particles producing the arc lines.†

These experiments suggested that centres of emission of different constitution were concerned in the production of the two classes of lines, but HEMSALECH hesitated to adopt this view until other experiments had been made.

The series investigation not only points to the existence of different emitting systems, but, in the light of BOHR'S theory, may possibly give a clue to the nature of the difference. The appearance of 4N in the formulæ for series of enhanced lines suggests that, as in the case of proto-helium, such series are produced during the binding of an electron by each of the atoms from which two electrons have been removed by the exciting source; while arc series lines are emitted during the re-formation of atoms from each of which only one electron has been removed. Although the neutral atoms of different elements contain different numbers of electrons, the approximate constancy of N for arc series, according to BOHR, is explained by the fact that the force on an electron entering a system consisting of a positive nucleus and a number of electrons one less than that required to render it neutral would not be very different from the force in the case of the binding of an electron by a hydrogen atom. A similar explanation would evidently account for the constancy of 4N in the formulæ for series of enhanced lines. Variations from the simple series conditions presented by hydrogen and proto-helium would be expected in consequence of the presence of additional electrons, but these have not yet been worked out theoretically by Dr. BOHR.

* 'Comptes Rendus,' vol. 151, pp. 220 and 668 (1910).

† 'Comptes Rendus,' vol. 154, p. 873 (1912).

The varying facility with which enhanced lines can be produced in the spectra of different elements would seem to depend upon the intensities of the forces which bind the electrons to the nuclei. In some elements, such as lithium, no enhanced lines at all have been observed. The lithium atom is credited with three electrons, and BOHR's calculations indicate that while the outer electron is lightly bound, the inner two are very strongly bound as compared with the electron in an atom of hydrogen, and even more rigidly than the two electrons in a helium atom. Theory and experiment are thus in agreement, and the production of enhanced lines of lithium would appear to require more powerful spark discharges than those hitherto employed.

In the case of elements like calcium, which give enhanced lines of Class I., it may be supposed that one electron is lightly bound, so that even a flame may effect its removal, while a second is removable by the moderate increase in the energy of excitation when passing from the flame to the arc. The further increase in the intensities of the enhanced lines on passing to the spark may be attributed to the relatively greater number of atoms from which two electrons are simultaneously detached. In elements like iron, giving enhanced lines of Class II., the conditions may be supposed similar, except that the second electron is removed with somewhat greater difficulty.

Enhanced lines like Mg 4481 require a modified explanation. Although the series to which this line belongs is produced only under spark conditions (or their equivalents in modified arcs) it is important to bear in mind that the related system of Wide doublets, consisting of enhanced lines of Class I., is developed in the ordinary arc. Since the term 4N appears in the formulæ for both systems, BOHR's theory would lead to the supposition that in this case the greater energy of the spark does not result in the separation of a third electron from any of the atoms but merely produces some change in the configuration of the atomic systems. The experimental data are not sufficiently complete to justify the conclusion that such an explanation would be applicable to all enhanced lines of Class III.

If, by any means, three electrons could be separated from the nucleus, the appearance of lines for which the series constant was raised to 9N would be expected, if BOHR's theory is a safe guide. Great energy would apparently be needed to bring about this result, and no such series have yet been recognised. A sufficient increase in the energy of excitation would presumably yield series requiring still greater multiples of the constant N in the formulæ.

It will be observed that BOHR's theory gives a more definite conception to LOCKYER's earlier view that the varying spectra given by the same substance represent the vibrations of different "molecular groupings," such groupings being simplified by successive dissociations brought about by increase of temperature or electrical excitation.

It should be noted that some of the conclusions drawn by STARK from his experiments on canal-ray spectra are inconsistent with the views of BOHR. In the case of helium, STARK has found that the Döppler displacements are smaller for the doublet series (helium group) than for the single line series ("parhelium" group), and he infers that the atoms which act as carriers in the former case have a single positive charge, while in the second case there is a double positive charge.* Both sets of series, however, are of the "arc" type, with N for the series constant, whereas on BOHR'S theory, one should be of the N, and the other of the 4N type if STARK'S deduction is correct.

In the case of aluminium, STARK has similarly found evidence of atoms with one, two, and three positive charges.† The first is associated with the doublets of the arc spectrum, the second with a spark line at 4663·5, and the third with three spark lines at 4529·7, 4513·0, and 4480·0. Attention is drawn to the fact that the higher charges are connected with the enhanced lines, and differences in the behaviour of the two sets of spark lines when the spark is passed in hydrogen are indicated. The series to which the spark lines of aluminium belong have not yet been recognised, but STARK'S results for this element are in general agreement with the conclusion indicated by BOHR'S theory that enhanced lines are associated with atoms of greater positive charges than those giving rise to arc lines. In the case of helium it does not seem possible to reconcile STARK'S conclusions with those of BOHR, since the doubly-charged atoms, on BOHR'S theory, can only give rise to the system of series of which 4686 is the leading member.

STARK'S conclusions are equally at variance with those of LENARD,‡ who found reason to believe that while principal series are produced by neutral atoms, the subordinate series originate in atoms which have become positively charged through the loss of one or more electrons. BOHR'S theory differs from both in leading to the conclusion that all series having the same series constant should be produced by atoms having the same charge.

A knowledge of the charges of the atoms giving the arc and enhanced lines respectively would possibly aid in the interpretation of the peculiarities of the spectrum of the solar chromosphere, and further investigations bearing on this subject are very desirable.

Whatever may be its significance in connection with the atom, the change in the character of the series in passing from arc to spark lines suggests the spectra of "early-type" stars as a possible source of series requiring still greater multiples of the ordinary series constant in the formulæ representing them. In passing from the later to the earlier type stars, as shown by the work of LOCKYER and others, the arc lines of various metallic elements are gradually replaced by enhanced lines, while lines of hydrogen, helium, and other gases become more prominent. For such metallic elements as are known to belong to series, the change is definitely from series of the arc (N) type to series of the spark (4N) type. A considerable number of lines remain without identification, but a preliminary examination of these has given no certain evidence of series for which the series constant would be 9N.

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* 'Ann. der Physik,' vol. 40, p. 540 (1913).

† 'Ann. der Physik,' vol. 42, p. 254 (1913).

‡ 'Ann. der Physik,' vol. 17, p. 197 (1905).

The Wolf-Rayet ("bright-line") stars are of special interest in this connection, as they are generally considered to represent the first stage in the condensation of nebulous matter into stars, and in many of them the proto-helium lines are a prominent feature. NICHOLSON has suggested that some of the lines may belong to series which can be represented, in wave-lengths, by the formula

$$\lambda = 3646 \frac{(m \pm \frac{1}{3})^2}{(m \pm \frac{1}{3})^2 - 4},$$

where 3646 is the limit of the hydrogen series.* The lines were regarded as a possible extension of the hydrogen spectrum, but on the supposition that other lines associated with them may coincide with the Balmer series, Dr. BOHR has pointed out that all the lines might be united in a single series and might be attributed to lithium. The binding of an electron by a lithium atom from which the three electrons have been removed would, on the theory, give rise to such a series, namely,

$$\lambda = 3646 \frac{m^2}{m^2 - 36},$$

or

$$n = 27418 - \frac{9 \times 109675}{m^2}.$$

This hypothetical series would thus be of the "9N" type, but its existence in this form is not confirmed by the observational data. Omitting the lines which would coincide with the ordinary lines of hydrogen, the earlier members of the series would be 5697, 5193, 4633, 4466, 4243, &c. Of these only the first, third, and fourth are possibly represented in the Wolf-Rayet stars, and since the intensities should degrade in regular order in passing from red to violet, the absence of a line at 5193 is conclusive proof that the observed lines do not form a series of the "9N" type.

In a further discussion of the spectra of the Wolf-Rayet stars, NICHOLSON has arranged most of the lines in a number of series of a different character, in which the Rydberg constant is replaced by various *fractional* parts of its value for hydrogen.† The numerical relations traced in this way are very striking, but the individual series indicated are very fragmentary, and such lines do not always occur together in the same star. The suggested series are also remarkable as involving different fractional values of the Rydberg constant for series proceeding to the same limit.

The general progression from series of the N type to those of the 4N type in passing through the stellar sequence would suggest that further change, if any, would be in the direction of multiples, rather than fractions, of N in the series formulæ. It is doubtful, however, whether any change beyond that represented by enhanced lines should be expected. It is now easy to produce a spectum in which the proto-helium line 4686 exceeds any of the ordinary helium lines in brightness, and from the persistence of the ordinary helium lines in many of the Wolf-Rayet stars it seems reasonable to infer that even in these stars the conditions are not indefinitely in advance of those obtainable in laboratory experiments.

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* 'Monthly Notices R.A.S.,' vol. 73, p. 382 (1913).

† 'Monthly Notices R.A.S.,' vol. 74, p. 118 (1914).

§ 14. *Summary.*

(1) The enhanced (spark) lines of magnesium, calcium, strontium, and barium form series of doublets which occur in groups similar to those previously recognised in arc spectra. The formulæ representing these series, however, differ from those employed for arc lines in that RYDBERG's constant "N" (= 109675 for ROWLAND's scale) has a value equal to 4N.

(2) The Fundamental series, in the Doublet systems of calcium, strontium, and barium, as shown by SAUNDERS and LORENSER, derives its limit and the separation of its components from an observed negative term of the Diffuse series. In the case of magnesium, the corresponding negative term of the Diffuse series, and the Fundamental series which might have been expected, do not exist.

(3) A new group of series of narrower doublets has been found in magnesium, in which the separation of the Sharp and Diffuse pairs is identical with the (calculated) separation of the *second* pair of the Principal series of wider doublets. The new group is designated the "F.P." system; in addition to the ordinary series it includes two well-marked combination series, each consisting of seven observed lines.

(4) The "4481" series of magnesium consists of very close doublets with constant separation, and forms the Fundamental series of the "F.P." system. Its limits are derived from the first negative term of the Diffuse series.

(5) Corresponding series of the "F.P." and Wide doublet systems run parallel to each other, but notwithstanding this numerical relation, the two systems do not necessarily co-exist, the wider doublets occurring in the ordinary arc as well as in the spark, while the "F.P." group occurs only under spark conditions or their equivalent in the region of the negative pole of an arc *in vacuo*.

(6) No numerical relations have been traced between any of the enhanced line series and the series of arc lines of the same element.

(7) The "4686" series produced in helium tubes is of the enhanced line (4N) type, and can no longer be considered to belong to the same group as the Balmer series of hydrogen, which is of the arc (N) type. It is concluded that these lines are due to helium, as indicated by Dr. BOHR from theoretical considerations. It is suggested that they should be designated "proto-helium" lines.

(8) Analogy with the "4481" series of magnesium indicates that the "4686" series

of proto-helium is primarily of the Fundamental type; the three associated series may be regarded as coincident with it.

(9) The "Pickering" lines associated with the "4686" series are also probably due to proto-helium, in which case the series would include lines nearly coincident with the Balmer series. The observational evidence on this point is incomplete, but the assignment of these lines to proto-helium is supported by the fact that one of the new combination series of magnesium is related to the "4481" series exactly as the extended Pickering series would be related to the "4686" series.

(10) The slight differences between the observed positions of alternate lines of the "4686" series and those calculated by RYDBERG for the "Principal" series of hydrogen are in very close agreement with BOHR's theoretical formulæ for hydrogen and proto-helium. Adopting these formulæ, the spectroscopic data give a provisional value for the mass of the hydrogen atom, in terms of that of the electron, as 1836 ± 12; or 1855 ± 12 when the data are corrected to the International scale of wave-lengths.

(11) The appearance of the Rydberg constant in enhanced lines series with four times its usual value may be explained on BOHR's theory by supposing that series of the arc type are produced when only one electron is removed from each of the atoms involved, while in the case of enhanced lines two electrons are removed.

(12) A preliminary examination of terrestrial and celestial spectra has given no indications of series requiring still greater multiples of the Rydberg constant in the formulæ representing them.

The author has pleasure in acknowledging his obligations to Mr. W. JEVONS, A.R.C.S., D.I.C., B.Sc., who has taken the new photographs of the magnesium spectrum, and has given much valuable assistance in other ways.

APPENDIX.

The wave-lengths (on the International scale) of the enhanced lines of magnesium, as observed in the arc *in vacuo* in the course of the foregoing investigation, are brought together in Table XVI. The letters indicating the series to which the lines belong have the significance given in the description of Plate 3. For completeness additional lines observed by LORENSER and by LYMAN are also included.

TABLE XVI.—Enhanced Lines of Magnesium.

λ (I.Å.).	Intensity.	Series.	Remarks.
			Derived from LORENSER'S values :—
7896·37	—	*d*	7896·63 Rowland scale
7877·13	—		7877·39 " "
6545·80	5	B	LORENSER 6546·77 " " 6545·66 " "
6346·67	5	A	" 6347·27 " "
5401·05	5	B	" 5401·2 " "
5264·14	5	A	" 5264·2 " "
4851·10	5	B	
4739·59	5	A	
4534·26	4	B	
4481·327	100	*f*	KING . . 4481·499 " "
·129			" . . ·284 " "
4436·48	5	A	
4433·991	8	*s*	
4427·995	7		
4390·585	10	*d*	
4384·643	8		
4331·93	3	B	
4242·47	4	A	LORENSER 4242·60 " "
4193·44	2	B	
4109·54	3	A	
4093·90	1	B	
4013·80	2	A	
3850·40	6	C	
3848·24	7		
3615·64	3	*p*	
3613·80	4		
3553·51	5	*s*	
3549·61	4		
3538·86	6	*d*	
3535·04	5		
3175·84	2	*s*	
3172·79	1		
3168·98	3	*d*	
3165·94	2		
3104·805	30	*f*	
·713			
2971·70	1	*s*	
2969·02	0		
2967·87	1	*d*	
2965·19	0		
2936·496	35	S	NACHEN (Arc) 2936·516 (I.Å.)
2928·625	35		" " 2928·636
2802·698	50	P	" " 2802·718
2797·989	40	D	" " 2798·016
2795·523	50	P	" " 2795·545
2790·768	40	D	" " 2790·801
2660·821	10	*f*	
·755			
2449·573	6	*f*	
2329·58	5	*f*	
2253·87	4	*f*	
2202·68	3	*f*	
2166·28	2	*f*	
		S	LYMAN . . . 1753·6 Rowland scale
			" . . . 1750·9 " "
		D	" . . . 1737·8 " "
			" . . . 1735·0 " "

Description of Plate.

The photographs are of the spectrum of the magnesium arc *in vacuo*. The letters indicate the series to which the lines belong, and have the following significance :—

Enhanced lines . .	P,	Principal series	Wide doublet system.
	D,	Diffuse ,,	
	S,	Sharp ,,	
	p,	Principal ,,	"F.P." doublet system.
	d,	Diffuse ,,	
	s,	Sharp ,,	
	f,	Fundamental series	
	A,	Combination ,, A	
	B,	,, ,, B	
	C,	Other combination lines	
Arc lines	R_1,	Rydberg series of single lines (Diffuse).	
	R_2,	,, ,, ,, ,, (Sharp).	
	T_1,	Diffuse series of triplets.	
	T_2,	Sharp ,, ,,	

1, 2, 3 show chiefly the two Combination series of enhanced lines and the "F.P." doublets near the Fundamental line λ 4481.

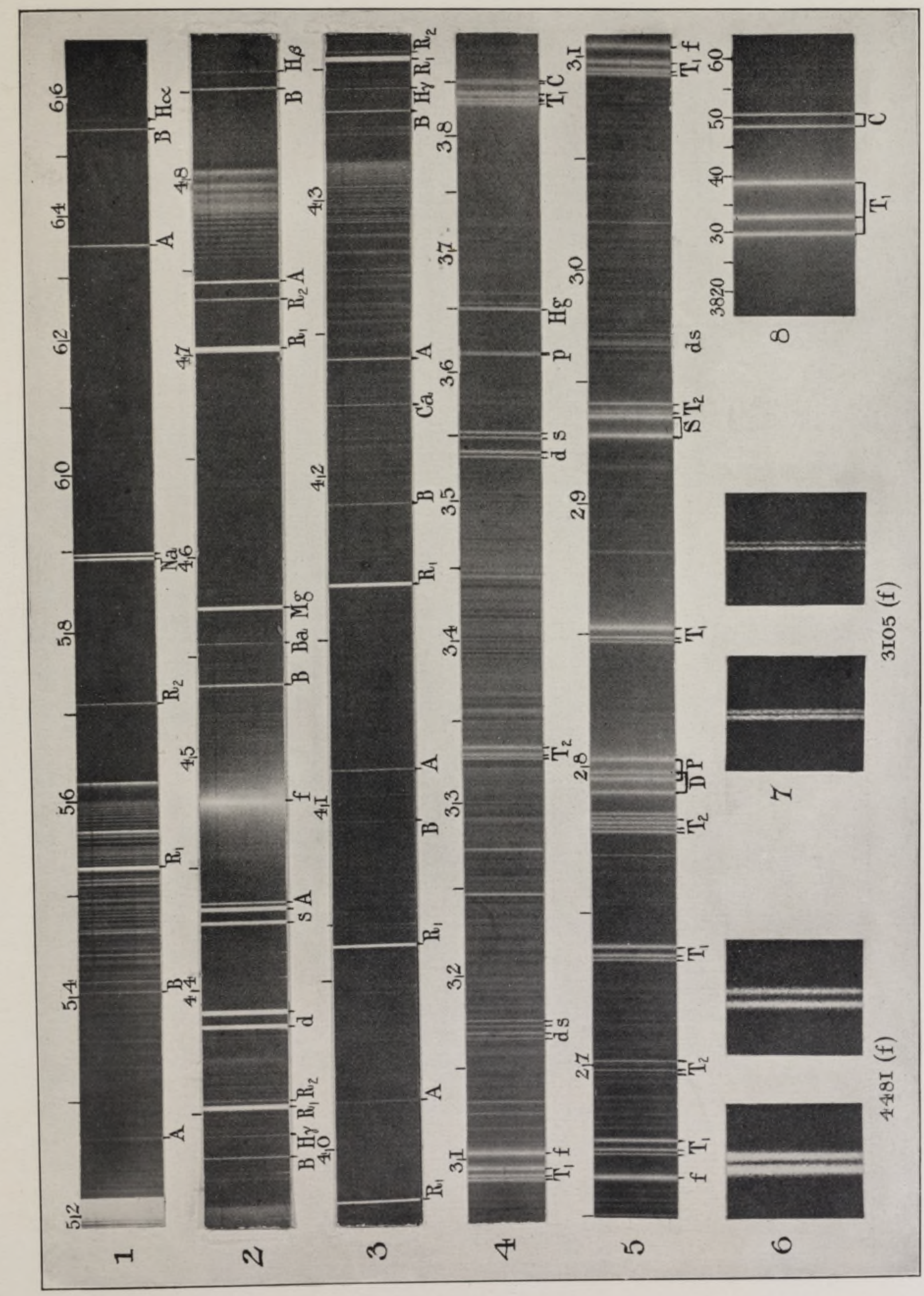
4, 5 show further members of the "F.P." system and the Wide doublets in the ultra-violet.

6, 7—Grating, 4th order—enlarged about eleven times. λ 4481 ($\delta\lambda = 0{\cdot}198$) and λ 3105 ($\delta\lambda = 0{\cdot}092$) respectively, each with a longer and a shorter exposure.

8, the "F.P." Combination doublet (λ 3850, λ 3848) near the Diffuse triplet.

Lines of impurities — Na, Hg, Ca, Ba, H.

Bands of magnesium hydride (5211, 4802).


1
2
3
4
5
6
7
8
5,2
5,4
5,6
5,8
6,0
6,2
6,4
6,6
A
B
R₁
R₂
Na
Hα
4,0
4,4
4,5
4,6
4,7
4,8
B Hγ R₁ R₂
d
s A
f
B
Ba
Mg
R₁ R₂ A
B Hβ
4,1
4,2
4,3
R₁
A
B
R₁
B
Ca
A
B Hγ R₁ R₂
3,1
3,2
3,3
3,4
3,5
3,6
3,7
3,8
T₁ f
d s
T₂
d s
p
Hg
T₁ C
2,7
2,8
2,9
3,0
3,1
f T₁
T₂
T₁
T₂
D P
T₁
S T₂
d s
T₁ f
4481 (f)
3105 (f)
3820
30
40
50
60
T₁
C

VI. *The Ultra-Violet Band of Ammonia, and its Occurrence in the Solar Spectrum.*

By A. Fowler, *F.R.S., Professor of Astrophysics, and* C. C. L. Gregory, *B.A., Research Student, Imperial College, South Kensington.*

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[Plate 2.]

Introductory.

A question of great interest in connection with the solar spectrum is that of the origin of the thousands of unidentified faint lines which were catalogued by Rowland in his "Preliminary Table of Solar Spectrum Wave-lengths." Some of these lines may possibly be identical with faint lines in metallic spectra which have not yet been completely tabulated, but in view of the presence of bands of cyanogen, carbon and hydrocarbon, the possibility of the correspondence of most of them with band spectra of other substances should not be overlooked.

As a contribution to this inquiry, the present investigation was undertaken primarily in order to determine whether Group P in the ultra-violet region of the solar spectrum might not be mainly due to the presence of ammonia in the absorbing atmosphere of the sun. Ammonia was already known to give a remarkable band in this region, having its position of maximum intensity near λ 3360, but it had not been investigated in sufficient detail to permit of an adequate comparison with the solar tables. Photographs have accordingly been taken with spectrographs of high resolving power for the purpose of this comparison, and, as will appear from the details which follow, it has been established that the ammonia band is certainly represented in the solar spectrum, and accounts for a considerable number of faint lines for which no other origins have been suggested.

In view of the unusual appearance of the band, an attempt has also been made to elucidate the chief features of its structure.

Previous Observations.

The characteristic ultra-violet band of ammonia, about λ 3360, appears to have been first described by Eder, who observed it in the flame of ammonia burning in

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oxygen.[*] Other bands in the ultra-violet which were attributed to ammonia by Eder were afterwards found to be identical with Deslandres' third positive group of bands of nitrogen. New determinations of the positions of the ammonia bands in the visible spectrum were also made by Eder, but it is not necessary to consider these for the present investigation. In the case of the ultra-violet band, the thirty-four wave-lengths tabulated by Eder evidently refer to unresolved groups of band lines, and only serve for identification when instruments of small resolving power are employed.

More recently, the band has been described and illustrated by Lewis, as it appears in the spectra of vacuum tubes containing mixtures of nitrogen and hydrogen.[†] Its occurrence was observed with these gases in any proportion, but not in the case of either gas alone. As obtained in this way, the band was complicated by superposed bands of nitrogen, and higher resolution than that employed was considered necessary to effect the separation satisfactorily.

The band in question has been noted occasionally in various experiments carried on at the Imperial College during several years. It has been observed in the flame of imperfectly dried cyanogen, in the spectra of vacuum tubes, and with enclosed arcs under reduced pressure, as well as in the ammonia flame itself. In all cases the band appeared under circumstances in which its presence could be attributed to combined nitrogen and hydrogen, but the spectroscopic evidence does not exclude the possibility of some combination other than ammonia. In the course of the present investigation it has further been found that the brighter parts of the band sometimes occur feebly in the spectrum of the copper arc, and even in that of the ordinary carbon arc in air.

Experimental Procedure.

A preliminary investigation was undertaken to find a source that would give the band sufficiently isolated, and at the same time bright enough to be photographed with high dispersion. Vacuum tube methods proved unsatisfactory on account of the superposition of bands of nitrogen. The purest band was obtained from an ammonia flame fed with oxygen. An ordinary blowpipe was found to be a convenient arrangement, ammonia being passed through the outer tube, and a stream of oxygen through the inner one. The apparatus employed is illustrated in fig. 1. Ammonia of specific gravity 0·880 contained in the flask A was heated by a Bunsen flame, but not sufficiently to cause the liquid to boil. The vessel B was introduced as a means of condensing most of the water vapour, which otherwise condensed in the tubes of the blowpipe and extinguished the flame. The mercury gauge at C provided a convenient means of measuring the pressure, which was maintained at about 10 cm. of mercury. Oxygen was supplied from a cylinder of the compressed gas. The flame produced in this way could be kept fairly steady, and had a small, but intensely bright, central core of a yellow colour, which was surrounded by a paler envelope. The flame was pointed in the direction of the collimator of the spectrograph, and an image of the bright central core was focussed on the slit by a quartz lens. Photographs were first taken with a small quartz spectrograph giving a dispersion of about 60A per millimetre at λ 3360, and with a quartz Littrow instrument giving a dispersion in the same region of 7A per millimetre.

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[*] 'Denkschr. Wien Akad.,' vol. 60, p. 1 (1893).

[†] 'Astrophys. Jour.,' vol. 40, p. 154 (1914).

In view of the need for the highest attainable resolution of the central parts of the band, an attempt was made to photograph the spectrum of the flame in the 3rd order of a 10-foot concave grating, in which the dispersion is 1·85A per millimetre. An exposure of 12 hours, however, yielded only a feeble trace of the band, and it was evident that very much longer exposures would be necessary to give satisfactory photographs for measurement. Difficulties were anticipated in maintaining steady instrumental conditions, as the regular mounting is still detained in Russia, and only a temporary arrangement of the grating was available.

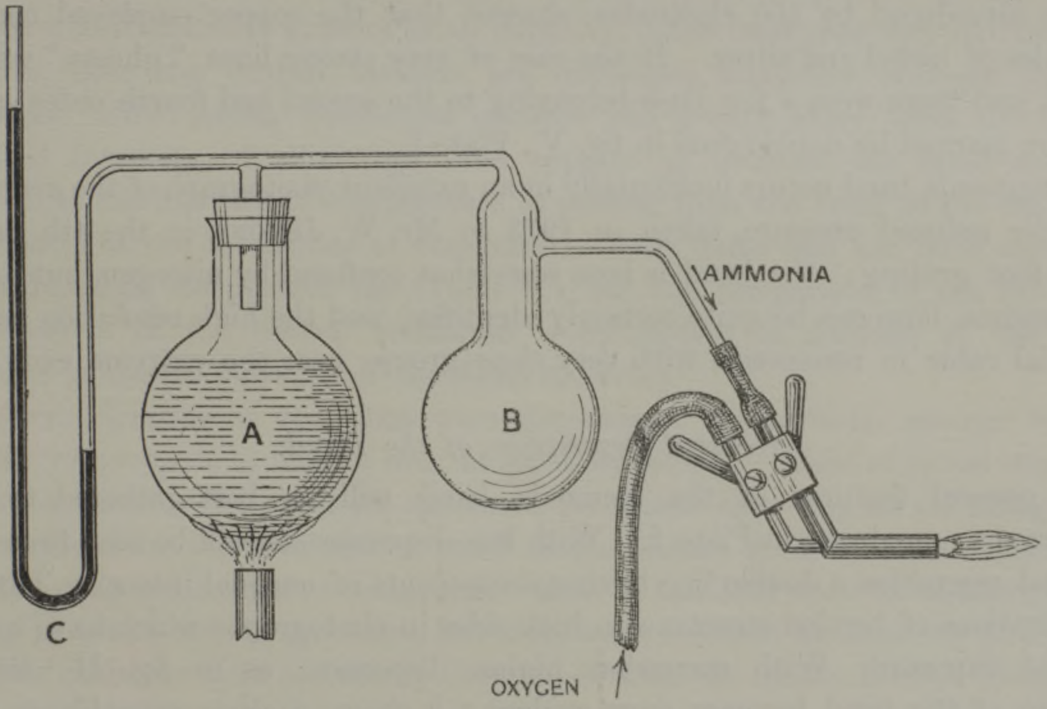

Fig. 1. Apparatus employed for ammonia flame.

Advantage was therefore taken of the possibility of producing the band in the electric arc, which had previously been noted in the course of experiments made for other purposes. In the first arrangement tried the arc was enclosed in a glass globe provided with side tubes for the admission of the electrodes, and with a quartz window through which the arc could be observed, as in a previous investigation on the spectrum of magnesium.* It was found, however, that the quartz window became obscured by the condensation of water-vapour, and it was therefore replaced by a metal disc having a small aperture through which the light of the arc could pass to the spectrograph. A constant stream of ammonia, which was drawn off by a water pump, was caused to flow through the apparatus. The arc was on a 200-volt circuit, and the current used was 1·8 amperes. The electrodes were of copper.

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* 'Phil. Trans.,' A, vol. 209, p. 449 (1909).

The grating was mounted so as to give a normal spectrum, and precautions were taken to avoid mechanical displacements. The temperature of the laboratory was also kept as constant as possible during the exposures, which were of about 60 minutes' duration. An internal shutter, detached from the other parts of the spectrograph, was arranged next the plate to allow of two comparison spectra being photographed, one before and one after the ammonia spectrum.

A photograph of the copper arc in air, which was taken to facilitate the elimination of lines introduced by the electrodes, showed that the copper employed contained impurities of nickel and silver. In the case of very strong lines, "ghosts" were also present, and there were a few lines belonging to the second and fourth order spectra; these are marked by double dots in fig. V., Plate 2.

The ammonia band occurs incidentally in an excellent photograph of the magnesium arc under reduced pressure, taken in 1913 by Mr. W. JEVONS, in the 4th order of the 10-foot grating; the band is here somewhat confused by nitrogen, but many of the ammonia lines can be quite certainly identified, and the high resolution has been of special value in connection with very close groups near the extreme ends of the band.

General Description of the Band.

The general features of the ammonia band will be best gathered from the photographs reproduced in Plate 2. With low dispersion, as will be seen from fig. I., the band resembles a double line having components of unequal intensity, but there are indications of banded structure on both sides in photographs which have received sufficient exposure. With somewhat higher dispersion, as in fig. II., the real structure of the band becomes more evident; it shows a closer resemblance to the ordinary type of band, such as those found in nitrogen, with the exception that the component lines fade off in both directions from the apparent head.

In fig. III., taken with the still higher dispersion of the quartz Littrow spectrograph, many of the band lines are resolved into groups of three, which cannot properly be called triplets on account of the variable spacing. The central maximum about 3360, however, remains imperfectly resolved. With the highest resolution employed—that of the 3rd order grating—additional groups of three are separated, and the central maximum is seen to consist of a great number of closely crowded lines (figs. IV. and V.). The secondary central maximum about 3371, which corresponds to the weaker component of the doublet which represents the band with low dispersion, is also resolved into a large number of component lines. It will be observed that while the central maximum degrades in both directions, the secondary maximum degrades only towards the red.

In the arc, the central and secondary maxima are more fully developed than in the flame, in the sense that the band lines extend to greater distances from the two heads. That the majority of the additional lines are really due to ammonia, and have not been introduced from other possible sources in the arc, is sufficiently proved by the series investigation, which shows that many of them are associated with the lines which appear in the flame. This greater development of the central parts of the band in the arc is accompanied by a weakening of the groups of three in the vicinity of the maxima, and a relative intensification of those further away.

Similar modifications have also been noted in the case of vacuum tube spectra when discharges of different intensity have been employed. No special experiments have been made in this connection, but in some photographs of the spectrum of nitrogen where ammonia appears as an impurity, it has been observed that the groups of three near the central maxima are developed relatively strongly by feeble discharges, while strong discharges enhance the groups away from the maxima. Increased intensity of discharge thus appears to produce the same change of spectrum as the increase of temperature in passing from the flame to the arc.

Estimates of the intensities of the lines in both flame and arc have accordingly been included in the general list (Table V.), but the comparison of the two sources in the region of the central maximum is incomplete on account of the smaller resolution in the photographs of the flame spectrum.

The wave-lengths of the lines were determined in the usual manner by interpolation with respect to lines of iron, as given by BURNS. Lines of nickel originating in the poles employed for the arc spectrum, for which wave-lengths are also given by BURNS, served for the detection of small displacements of the reference spectra, and to indicate the corrections to be applied. Most of the lines could be measured on the grating plates of the arc spectrum, but some were obscured by lines due to the poles, and their positions were necessarily determined from the quartz Littrow photographs of the flame spectrum. It is hoped that in most cases the wave-lengths are accurate to within 0·01A.

Details of the wave-lengths and intensities are included in Table V.

Structure of the Band.

The Groups of Three.—A considerable amount of regularity in the structure of the ammonia band is obvious by mere inspection of the photographs. This is especially the case with regard to the groups of three, which extend for more than 70A on each side of the central maximum. There are three series on the less refrangible side which coalesce towards the red, and three on the more refrangible side which coalesce towards the violet. To facilitate discussion, those on the less refrangible side have been designated α, β, γ, and those on the more refrangible side δ, ϵ, ζ, in order of increasing refrangibility in the groups of three in each case.

Data for the consideration of the regularity in these series are collected in Tables I. and II., the first referring to α, β, γ, and the second to δ, ϵ, ζ. The wave-

TABLE I.—The Series α, β, γ.

α series.				β series.				γ series.			
λ, I.A.	ν, vac.	d_1.	d_2.	λ, I.A.	ν, vac.	d_1.	d_2.	λ, I.A.	ν, vac.	d_1.	d_2.
3450·36	28,974·34			3450·36	28,974·34						
		28·33				28·33					
46·99	29,002·67		−3	46·99	29,002·67		−2				
		28·05				28·13					
43·66*	030·72		−3	43·65*	030·80		−3				
		27·77				27·85					
40·37*	058·49		0	40·35*	058·65		1	3440·33	29,058·82		
		27·81				27·91				28·23	
37·08*	086·30		1	37·05*	086·56		1	36·99	087·05		1
		27·95				28·03				28·30	
33·78	114·25		1	33·74	114·59		2	33·65	115·35		1
		28·00				28·25				28·43	
30·48	142·25		3	30·41	142·84		2	30·30	143·78		2
		28·32				28·40				28·66	
27·15	170·57		1	27·07	171·24		4	26·93	172·44		3
		28·45				28·80				28·97	
23·81	199·02		4	23·69	200·04		3	23·53	201·41		2
		28·86				29·12				29·20	
20·43	227·88		1	20·28	229·16		1	20·11	230·61		3
		29·00				29·17				29·52	
17·04	256·88		1	16·87	258·33		3	16·66	260·13		3
		29·13				29·49				29·84	
13·64	286·01		2	13·43	287·82		4	13·18	289·97		4
		29·37				29·89				30·22	
10·22	315·38		2	09·95	317·71		4	09·66	320·19		3
		29·60				30·28				30·47	
06·78	344·98		3	06·43	347·99		2	06·12	350·66		4
		29·92				30·44				30·88	
3403·31	374·90		3	3402·90	378·43		3	3402·54	381·54		3
		30·24				30·78				31·20	
3399·81	405·14		2	3399·34	409·21		3	3398·93	412·74		5
		30·39				31·09				31·72	
96·30	435·53		2	95·75	440·30		4	95·27	444·46		2
		30·54				31·50				31·93	
92·78	466·07		3	92·12	471·80		3	91·58	476·39		7
		30·85				31·83				32·64	
89·23	496·92		−1	88·46	503·63		4	87·84	509·03		2
		30·76				32·25				32·87	
85·70	527·68		−1	84·76	535·88		3	84·07	541·90		8
		30·64				32·50				33·65	
82·19	558·32		−2	81·04	568·38		6	80·22	575·55		8
		30·44				33·09				34·43	
78·71	588·76		−8	77·26	601·47		13	76·29	609·98		16
		29·63				34·40				35·99	
75·33	618·39		−21	73·34?	635·87			72·19?	645·97		
		27·58									
72·19?	645·97										

* Unresolved; separations assumed.

TABLE II.—The Series δ, ϵ, ζ.

δ series.				ϵ series.				ζ series.			
λ, I.A.	ν, vac.	d_1.	d_2.	λ, I.A.	ν, vac.	d_1.	d_2.	λ, I.A.	ν, vac.	d_1.	d_2.
3358·04 ?	29,970·85										
		39·19									
53·63	810·04		29	3350·85	29,834·77						
		36·31				28·79					
49·55	846·35		13	47·62	863·56		− 20	3346·42	29,874·26		
		35·06				30·80				28·68	
45·62	881·41		11	44·17	894·36		− 4	43·21	902·94		− 13
		33·99				31·23				30·00	
41·82	915·40		7	40·68	925·59		− 1	39·86	932·94		− 2
		33·33				31·30				30·23	
38·10	948·73		7	37·19	956·89		1	36·49	963·17		− 2
		32·59				31·18				30·39	
34·47	29,981·32		5	33·72	29,988·07		1	33·11	29,993·56		1
		32·14				31·06				30·26	
30·90	30,013·46		6	30·27	30,019·13		4	29·75	30,023·82		1
		31·57				30·68				30·15	
27·40	045·03		7	26·87	049·81		5	26·41	053·97		4
		30·91				30·20				29·77	
23·98	075·94		6	23·53	080·01		5	23·12	083·74		5
		30·34				29·72				29·26	
20·63	106·28		8	20·25	109·73		6	19·89	113·00		6
		29·58				29·13				28·67	
17·37	135·86		6	17·04	138·86		6	16·73	141·67		5
		29·00				28·55				28·20	
14·18	164·86		8	13·90	167·41		8	13·63	169·87		8
		28·16				27·79				27·43	
11·09	193·02		9	10·85	195·20		9	10·62	197·30		8
		27·29				26·93				26·65	
08·10	220·31		9	07·90	222·13		9	07·70	223·95		8
		26·42				26·07				25·89	
05·21	246·73		9	05·05	248·20		9	04·87	249·84		10
		25·55				25·18				24·91	
3302·42	272·28		12	3302·30	273·38		11	3302·15	274·75		10
		24·40				24·13				23·96	
3299·76	296·68		11	3299·67	297·51		11	3299·54	298·71		11
		23·26				23·07				22·88	
97·23	319·94		11	97·16	320·58		13	97·05	321·59		13
		22·17				21·81				21·62	
94·82	342·11		15	94·79	342·39		14	94·70	343·21		14
		20·67				20·46				20·19	
92·58*	362·78		15	92·57*	362·85		13	92·51	363·40		12
		19·17				19·19				19·01	
90·50*	381·95		13	90·49*	382·04		15	90·45	382·41		
		17·83				17·74					
88·57	399·78		18	88·57	399·78		17				
		16·00				16·00					
86·84	415·78			86·84	415·78						

* Unresolved; separations assumed.

length on the international scale (λ, I.A.), the wave number *in vacuo* (ν), and the first and second differences (d_1 and d_2) are shown for each series. The figures in the second decimal place in ν and d_1 are entitled to but little weight, but they have been included for the more consistent determination of d_2, which is given in tenths. The observed positions of some of the unresolved $\alpha\beta$ and $\delta\epsilon$ pairs are replaced by estimated positions of the components, in order that the course of the series may be more completely traced.

When due allowance is made for irregularities in the second differences, which are very sensitive to small errors in the wave-lengths, it is clear that the series as a whole cannot be satisfactorily represented by the usual approximate formula $\nu = a+b(m+\mu)^2$. Such a formula represents a series in which the distances between successive lines (d_1) are in arithmetical progression, so that the second differences (d_2) would be constant, and not one of the series approximates closely to this condition.

The actual wave-numbers of the members of the different series could only be effectively plotted on a very large scale, but the peculiarities of the series can be shown better in some respects by curves which have d_1 for ordinates, and successive integral values of m for abscissæ, the initial value of m being chosen arbitrarily. Such curves are shown in fig. 2, and it will be seen that they depart widely from the linear form implied by the above-mentioned formula. The curves also fail to show any symmetry in the arrangement of the groups of series on the two sides of the central maximum, such as might have been expected from the general appearance of the spectrum.

Considering the series α, β, γ, it will be seen that they begin with coincident, or nearly coincident, faint lines on the red side, and that the distance from line to line at first diminishes slightly and then increases. In β and γ the subsequent increase is continuous, so far as the series can be identified, and if the later lines have been correctly assigned, no other members in the immediate neighbourhood are to be expected. In the α series, the distance d_1 passes through a maximum value, as in the case of the main series of λ 3883 cyanogen which has recently been further discussed by BIRGE.* The α curve, however, differs from the cyanogen curves in having a double curvature, and while the greatest value of d_1 occurs among the weaker lines near the end of the series in cyanogen, it occurs among the brighter members in ammonia α. The later portion of the α curve is rather steep, and the identification of the next member of the series, which is involved in the secondary central maximum, is consequently difficult; the line λ 3372·19 (ν 29645·97), however, fits fairly well on the continued curve, and if this really belongs to the series it would probably be the last member.

The series δ, ϵ, ζ, resemble the first three in commencing with faint unresolved lines, which are far removed from the central maximum, but the d_1-m curves show no change of curvature near the beginning of the series. In the δ series the distance between successive lines increases continuously as the central maximum is approached, but in ϵ and ζ it passes through a maximum as in α.

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* 'Astrophys. Jour.,' vol. 46, p. 85 (September, 1917).

Birge has found a hyperbolic relation between d_1 and m in the case of cyanogen, but it does not seem that this is applicable to the series under consideration, with the possible exception of ϵ and ζ. While it is possible to give approximate formulæ of the usual type for these series over a large part of their ranges, there seems little hope at present of finding any accurate formula which can be adapted to all of them. One can hardly resist the conclusion that there is some connection between the groups of three and the central maxima, but no numerical relation has yet been established.

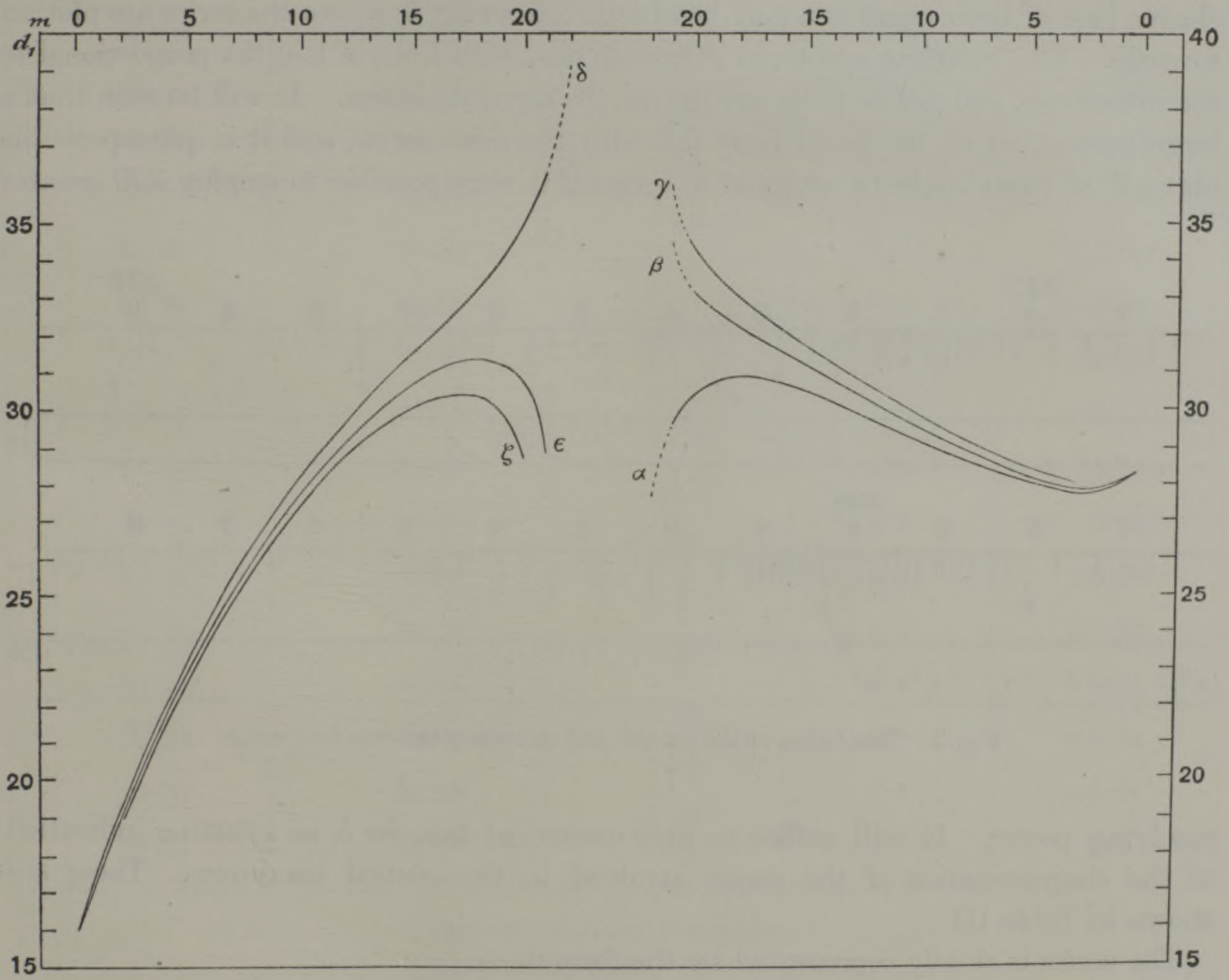

Fig. 2. Curves representing the varying distances between successive lines in the series α to γ. (The dotted portions of the curves are somewhat doubtful.)

It should be noted that in addition to the main series formed from the groups of three, there are other fragmentary series of fainter lines having intervals between successive lines of the same order of magnitude as those of the main series. These are indicated in the general table by α', α'', and δ'.

The Central Maxima.—The series which constitute the central and secondary maxima, so far as they have been identified, do not appear to present any unusual features. In each case there are several superposed series, and some of the lines, which are probably unresolved composites, have to be assigned to two or more series. The probable series belonging to the secondary maximum have been designated a_1, a_2, a_3, and a_4; those on the red side of the chief maximum b_1 and b_2; and those on the more refrangible side of the chief maximum c_1, c_2, and c_3. There is some uncertainty as to the c series, as alternative arrangements of the lines appear to be consistent with series relationships.

The lines belonging to the various series are indicated in the general table, but a clearer idea of their character may be obtained from fig. 3, where the series are plotted to scale. The complete spectrum is first shown, with lines of lengths proportional to the intensities, and below these are drawn the separate series. It will be seen that a large proportion of the band lines fall into the nine series, and it is quite probable that all of them could be assigned to series if it were possible to employ still greater

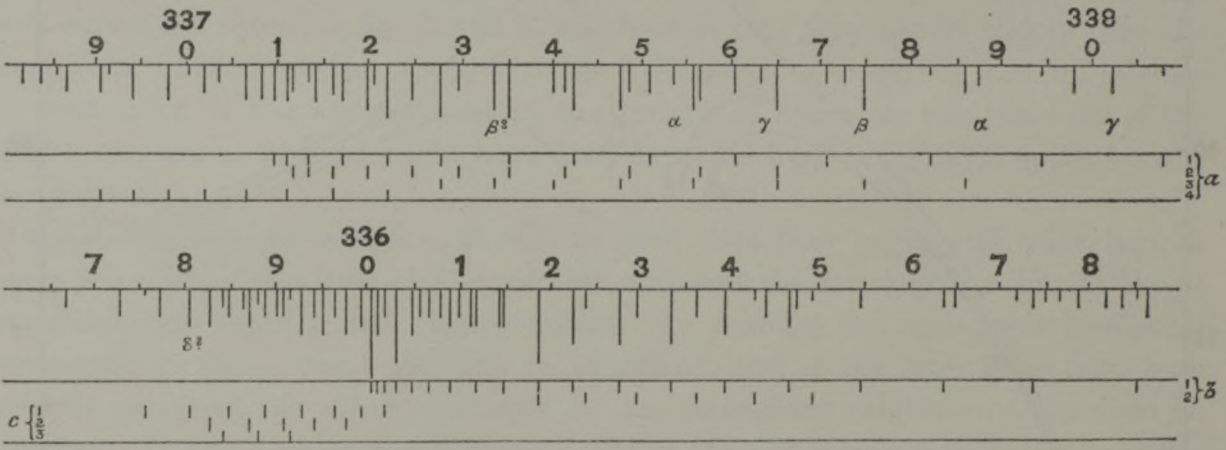

Fig. 3. Resolution of the central and secondary maxima into series.

resolving power. It will suffice to give numerical data for b_1 as a further indication of the characteristics of the series involved in the central maximum. These are shown in Table III.

The series is closely represented by the formula—

$$\nu = 29755{\cdot}176 - 0{\cdot}6935m + 0{\cdot}03327m^2 - 0{\cdot}008326m^3.$$

where m has values ranging from 3 to 21. The greatest deviation in wave-number is 0·41, corresponding to a difference of 0·045A between the observed and calculated values. The differences between the observed and calculated wave-numbers are shown in the last column of the table, and it will be seen that they are sufficiently systematic to indicate the imperfection of the formula. There would be no difficulty in calculating such formulæ for the other series, but it is not clear that they would serve any immediately useful purpose.

TABLE III.—Series b_1 of the Central Maximum.

λ, I.A.	ν, vac.	d_1.	d_2.	O – C.†
3368·53	29678·18			0·00*
		10·14		
67·38	88·32		1·2	+0·31
		8·99		
66·36	97·31		1·0	+0·41
		7·95		
65·46	29705·26		0·9	+0·35
		7·06		
64·66	12·32		0·8	+0·22
		6·28		
63·95	18·60		0·7	+0·11
		5·56		
63·32	24·16		0·6	0·00*
		4·95		
62·76	29·11		0·5	– 0·03
		4·42		
62·26	33·53		0·7	+0·04
		3·72		
61·84	37·25		0·5	– 0·01
		3·27		
61·47	40·52		0·5	+0·03
		2·75		
61·16	43·27		0·5	+0·03
		2·29		
60·90	45·56		0·3	0·00*
		1·95		
60·68	47·51		0·2	+0·02
		1·77		
60·48	49·28		0·3	+0·18
		1·50		
60·31	50·78		0·4	+0·37
		1·06		
60·19	51·84		0·3	+0·34
		0·80		
60·10	52·64		0·3	+0·24
		0·53		
60·04	53·17			0·00*

* Used in calculation of constants.

† O – C is expressed in wave-number.

Comparison with the Solar Spectrum.

Details of the comparison with the solar spectrum are included in the general catalogue of ammonia band lines given in Table V. To facilitate the comparison, the wave-lengths of the ammonia lines have been corrected to the scale of ROWLAND by the addition of 0·14A, as shown in the fifth column. The entries under "sun" are taken directly from ROWLAND's table, and in the densest region of the central maximum, extending from 3363·5 to 3358·0, the solar lines have been tabulated in full. A direct comparison of the two spectra in the neighbourhood of the central maximum is given in fig. 5, Plate 1, where the ammonia spectrum is reproduced as a negative in order to represent its appearance in absorption.

The comparison is complicated by the approximate coincidences of many of the ammonia lines with lines of metallic origin in the solar spectrum, or with unidentified lines which have intensities too great to allow of their being assigned to ammonia alone. As ROWLAND's limit of resolution appears to be about 0·04A, ammonia lines may evidently be masked in this way by solar lines showing considerable differences in wave-length. Direct evidence of the presence of all the ammonia lines in the sun, such as would be afforded by identity of wave-lengths throughout, is therefore not to be expected.

There is also some uncertainty as to the completeness of ROWLAND's list of wave-lengths, and as to the uniformity of his estimates of intensity. In this connection, a photograph of the solar spectrum in the HIGGS' collection of the Royal Astronomical Society has been to some extent utilised as a general check on ROWLAND in the region of the ammonia band. While the tabulated intensities on the whole were closely confirmed, there are several lines for which ROWLAND's estimates appear to need revision. Attention is drawn to some of these in the column of remarks in Table V. As regards the wave-lengths, the relation between the international scale and the scale of ROWLAND is by no means simple. Comparison of the solar lines with the positions on the international scale given for the iron and nickel lines by BURNS shows that whilst the average difference in the region of the ammonia band is about 0·14A, there is no consistent agreement among the different lines. Deviations from the mean in a selected region frequently amount to nearly 0·01A, and there are occasional variations of 0·02A and upwards. These irregularities are not necessarily due wholly to errors of measurement, but may also be caused by differences in the effective level at which the various lines are produced in the solar atmosphere. It would seem, however, that if due regard be paid to intensities, coincidences within 0·02A may not be without significance.

Notwithstanding the difficulties affecting the comparison, there is abundant evidence that the ammonia band is present in the solar spectrum. The most convincing proof is perhaps afforded by the strongest part of the central maximum, extending from 3360·45 to 3360·08 (ROWLAND's scale). As will be seen from fig. V., Plate 2, and from Table V., there is a complete correspondence of the solar and laboratory spectra as regards this group, except that the line 3360·45 may be slightly reinforced in the sun by a line of nickel.* This agreement is emphasised by the presence of a background of dark continuous spectrum which is sharply bounded in each of the two spectra by the outer two of the five lines involved. There is a similar dark ground covering the adjacent group 3360·82 to 3360·63, which is also clearly common to the two spectra.

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* A nickel line in this position is given by ROWLAND, but not by EXNER and HASCHEK.

The coincidences in the case of the central maximum as a whole are scarcely less striking. The majority of the solar lines in this region in fact appear to be due to ammonia, as will be seen from the table, where the solar lines from 3363·4 to 3358·0 are tabulated in full in order to bring out this feature. In this small region there are 47 solar lines, at an average distance apart of 0·117A, and 37 ammonia band lines, at an average distance of 0·149A. Thirty-four of the ammonia lines are either represented directly by reasonably appropriate lines in ROWLAND's table, or fall upon solar lines of recognised or probable metallic origins. The absence of one of the remaining three lines is satisfactorily accounted for by its low intensity. In the case of the outstanding lines 3361·61 and 3359·89, the solar line corresponding to the first appears to be masked by dark ground extending between the adjacent solar lines, while the second is probably included in the nebulous line 3359·936. The coincidences are clearly too numerous and too systematic to be considered accidental.* Confirmative evidence of their reality is afforded by the identity of narrow bright interspaces in the two spectra, especially those at 3361·0, 3360·9, 3360·5, 3360·0, 3359·7, and 3359·5, which will be clearly seen on reference to the photographs, these appear to be produced by patches of continuous background which are common to the two spectra. The discussion of the central maximum may thus be considered to establish the presence of ammonia in the sun beyond all doubt.

Analysis of the secondary maximum, occupying the region 3371 to 3378, leads to a similar conclusion, and there can be no doubt that the majority of the coincidences of lines of ammonia with faint solar lines in this part of the spectrum also have a real significance.

As regards the groups of three, forming the series α to ζ, there is also a close general agreement, and the few irregularities may well be caused by imperfect estimates of the wave-lengths and intensities in the two spectra, or by the approximate superposition of lines of other substances. If it were not for interference by metallic lines in the case of the sun, a good test would be provided by the series investigations. Supposing the coincidences to be genuine, the wave-lengths of the solar lines should show the series relations with the same order of accuracy as those of the ammonia lines themselves, and the intensities of the lines should be consistent with the series relationship. This test cannot be completely applied to any one of the six series, on account of near coincidences with metallic lines, but it may be worth while to take the chief lines of the δ series as an illustration. The facts with regard to these are collected in Table IV.

It will be observed that while three of the metallic lines (3341·967, 3320·783,

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* In order to get a rough idea of the proportion of coincidences which might be merely accidental, the 37 ammonia wave-lengths in the region 3363·5 to 3358·0 were compared with the 47 solar lines from 3563·5 to 3558·0. The total number of approximate coincidences was 14, as compared with 34 in the true region, and of these, 5 were with lines assigned to metals. There was no systematic agreement of intensities in this case.

TABLE IV.—Evidence for δ Series in the Solar Spectrum.

Ammonia.				Sun.				
Intensity in arc.	λ (ROWLAND).	d_1.	d_2.	Origin.	Intensity.	λ.	d_1.	d_2.
4	3349·69				00	3349·695		
		3·93					3·934	
4	45·76		13		00	45·761		140
		3·80					3·794	
4	41·96		08	Ti	4	41·967		074
		3·72					3·720	
4	38·24		09		0	38·247		086
		3·63					3·634	
4	34·61		06		0	34·613		077
		3·57					3·557	
5	31·04		07		1N	31·056		034
		3·50					3·523	
5	27·54		08	Ni	2	27·533		119
		3·42					3·404	
5	24·12		07		0	24·129		058
		3·35					3·346	
4	20·77		09	Mn, Fe	2	20·783		077
		3·26					3·269	
3	17·51		07		0	17·514		089
		3·19					3·180	
3	14·32		10	Mn	0	14·334		084
		3·09					3·096	
3	11·23		10		0	11·238		097
		2·99					2·999	
3	08·24		10		0N	08·239		114
		2·89					2·885	
2	05·35				000	05·354		

3314·334) produce no appreciable disturbance of the first and second differences, some disturbance is caused by the unidentified line 3331·056, and by the nickel line 3327·533. If, however, the former be assumed to include a line shorter in wave-length by only 0·016A, and the latter to include a line of wave-length greater by 0·010A, the series connection would be shown as accurately by the solar lines as by those of ammonia.* The probable composite character of 3331·056 is in fact suggested by its nebulous appearance, and by its intensity being too great to allow of its being assigned wholly to ammonia. The agreement in the intensities is also satisfactory on the whole. The series investigation, so far as it goes, thus confirms the identification of some of the solar lines with band lines of ammonia. A general consideration of the intensities of the representatives of the α to ζ series in the solar spectrum appears to indicate a closer agreement with the arc than with the flame spectrum, the lines in the neighbourhood of the central maximum being relatively enfeebled in each case. This is in accordance with the fact that all the brighter lines composing the central and secondary maxima as seen in the arc, some of which do not occur in the flame, are represented in the solar spectrum.

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* The second differences 077, 034, 119, 058 would then become 061, 076, 083, 068.

The outcome of the comparison is to show that of the 260 band lines of ammonia in the region λ 3450 to λ 3286, there are about 140 which correspond with previously unidentified faint lines in the solar spectrum. About 100 of the remaining lines are obscured by lines for which metallic origins have been found, or fall upon lines which are too strong in the sun to be attributed entirely to ammonia, and the few which fail to appear in the sun are all of low intensity.

It may be that additional solar lines are identical with lines composing the bands of ammonia which appear in the visible spectrum, but there are at present no experimental data for effective comparison.

Description of Table V.

The first five columns of the table give details of the ammonia band lines, showing the series to which they have been assigned, the intensities in the flame and arc, and the wave-lengths on the international and Rowland scales. The following three columns show the wave-lengths, intensities, and origins of solar lines occupying about the same positions as the ammonia lines, as given by Rowland. Between λ 3363·5 and λ 3358·0 all the solar lines are tabulated, in order to show the large proportion due to ammonia in the region of the central maximum of the ammonia band. In the column of remarks, the following references have been adopted to avoid repetition.

(1) Solar line probably not wholly due to ammonia, as indicated by excessive intensity.

(2) Intensity of solar line probably over-estimated by Rowland, as inferred from a Higgs' photograph.

(3) Very close ammonia lines, which are only vaguely resolved in the 3rd order of the 10-foot grating.

It should be noted that the resolving power in the case of the flame was less than that in the case of the arc spectrum.

TABLE V.—Catalogue of Ammonia Band Lines, with Solar Comparisons.

Ammonia.					Sun.			Remarks.
Series.	Intensity.		Wave-length.		λ Rowland.	Intensity.	Origin.	
	Flame.	Arc.	I.A.	Rowland.				
α, β		0	3450·36	3450·50	3450·469	5	Fe	
α, β		1	46·99	47·13	47·154	00N		
α, β		1	43·65	43·79	43·791	5*d* ?	Co	
α, β	0	2	40·36	40·50	40·505	0N		
γ		0	40·33	40·47				
α, β	1	3	37·06	37·20	37·190	3	Fe	
γ		0	36·99	37·13	37·116	000N		
α	1	2	33·78	33·92	33·905	0N		
β		2	33·74	33·88				
γ		1	33·65	33·79				
α	2	2	30·48	30·62				Probable faint solar line on edge of Zr 30·671.
β		2	30·41	30·55	30·545	00N		
γ		1	30·30	30·44	30·428	00		
α	2	2	27·15	27·29	27·263	3	Fe	
β		2	27·07	27·21	[27·220]	00		Solar line from HIGGS.
γ		1	26·93	27·07	27·046	0000		
α	3	2	23·81	23·95	23·972	0N		(2).
β		2	23·69	23·83	23·848	7	Ni	
γ		2	23·53	23·67	23·667	00N		
α	3	3	20·43	20·57	20·575	0		(2).
β		3	20·28	20·42	20·417	00		
γ	2	3	20·11	20·25	20·240	00		
α	4	3	17·04	17·18	17·198	00		
β		3	16·87	17·01	17·001	00		
γ	3	3	16·66	16·80	16·808	0		
α	4	4	13·64	13·78	13·782	0		
β		4	13·43	13·57	13·597	2	Ni	Not Ni in ammonia arc.
γ	3	3	13·18	13·32	13·275	5*d* ?	Fe	Ammonia may be included in solar lines.
α	3	4	10·22	10·36	10·386	1	Zr	
β	3	4	09·95	10·09	10·080	00		
γ	3	3	09·66	09·80	09·803	0		(2).
α′	00		09·20	09·34	09·346	2	Fe	
α	3	4	06·78	06·92	06·943	5*d* ?	Fe	
β	3	4	06·43	06·57	06·572	3	Fe	
γ	3	3	06·12	06·26	06·254	00		
α′	00		05·43	05·57				
α	4	4	03·31	03·45	03·478	2	Fe, Ti	
β	4	4	02·90	03·04	03·033	0		
γ	4	4	02·54	02·68	02·685	0		
α″	00		02·21	02·35	02·352	000		
α′	00		01·66	01·80	01·778	0000N		
α	5	4	3399·81	3399·95	3399·942	0N		
β	5	4	99·34	99·48	99·489	3	Fe	
γ	4	4	98·93	99·07	99·059	0		
α″	00		98·43	98·57	98·551	0000N		
α′	00		97·86	98·00				
α	6	4	96·30	96·44	96·437	0		
β	6	4	95·75	95·89	95·882	0		

TABLE V.—Catalogue of Ammonia Band Lines, with Solar Comparisons (continued).

Ammonia.					Sun.			Remarks.
Series.	Intensity.		Wave-length.		λ ROWLAND.	Intensity.	Origin.	
	Flame.	Arc.	I.A.	ROWLAND.				
γ	4	4	3395·27	3395·41	3395·408	00N		
α''	00		94·64	94·78	94·746	3	Fe	
α'	00		93·99	94·13				
α	6	4	92·78	92·92	92·926	0	Ti	Not given as Ti by KILBY.
β	6	4	92·12	92·26	92·259	0		
γ	5	4	91·58	91·72	91·726	0		
α'	0	0	90·07	90·21				
α	6	5	89·23	89·37	89·387	00		
β	6	5	88·46	88·60	88·604	0N		
γ	5	5	87·84	87·98	87·988	5*d* ?	Ti, Zr.	
	0N		87·27	87·41				
	00	2	86·55	86·69	86·691	00N		
α'	0	1	86·13	86·27				
		1	85·87	86·01	86·005	0000N		
α	6	5	85·70	85·84	85·861	00	Fe ?	
	0	1	85·24	85·38	85·361	3	Co	
β	5	5	84·76	84·90	84·908	1		(1).
γ	4	5	84·07	84·21	84·225	00		
α, a_1	7	4	82·19	82·33	82·340	0		
β	5	3	81·04	81·18	81·202	0000		Corrected solar $\lambda = 81 \cdot 170$.
a_1		1	80·78	80·92	80·889	1	Sr ?	
γ	4	3	80·22	80·36	80·397	3	Ti	
a_3		3	79·80	79·94	79·961	3	Cr	
a_1		1	79·43	79·57	79·577	000		
	0		79·25	79·39				
α	6	2	78·71	78·85	78·824	2	Fe	
a_3		3	78·58	78·72	78·723	00		
a_1		1	78·18	78·32	78·320	00		
a_3		5	77·48	77·62	77·622	3	Ti	
β	5	2	77·26	77·40	77·408	00		
a_1		2	77·04	77·18	77·202	0N	Co	
a_2, a_3		5*d* ?	76·48	76·62	76·630	2	Fe	
γ	4	2	76·29	76·43	76·414	0		(1).
a_1		3	76·01	76·15	76·164	00		
a_2		4	75·62	75·76	75·768	000		Arc includes faint Cu } (3).
a_3		5	75·57	75·71	75·698	1	Ni	,, ,, ,, Ni }
α	6	2	75·33	75·47	75·478	0N		
a_1		3	75·08	75·22	75·231	00		
a_2		3	74·84	74·98	74·981	000		
a_3	0	5	74·75	74·89	74·872	1	Zr	
a_1		5	74·23	74·37	74·358	4	Ni	Arc includes faint Ni.
a_2		3	74·14	74·28	74·271	000		
a_3		3	74·00	74·14	74·119	2		(1).
a_1, a_2		6	73·50	73·64	73·642	0		
a_3, β ?	5	5	73·34	73·48	73·452	0		Solar line probably double.
		0	73·12	73·26				
a_2		3	72·95	73·09	73·105	0N		(1).

TABLE V.—Catalogue of Ammonia Band Lines, with Solar Comparisons (continued).

Ammonia.					Sun.			Remarks.
Series.	Intensity.		Wave-length.		λ ROWLAND.	Intensity.	Origin.	
	Flame.	Arc.	I.A.	ROWLAND.				
a_1, a_3	2	6*d* ?	3372·77	3372·91	3372·901	5	Ti, Pd	
a_2		4	72·46	72·60	72·609	00N	Fe	
a_1, a_4	6	6*d* ?	72·19	72·33	72·314	0		Also series α ?, γ ?
		2	72·06	72·20	72·225	1	Fe	
a_2		5	71·99	72·13	72·124	4	Ni, —	Arc includes faint Ni.
a_1	1	4	71·71	71·85	71·852	00		
a_2, a_4		3	71·61	71·75	71·745	000		
		4	71·39	71·53	71·535	00		Difficult group in arc, which includes a faint metallic line.
a_1, a_2	1	?	71·34	71·48				
a_2		3	71·15	71·29	71·296	00		
a_1, a_4		4	71·10	71·24	71·246	00		
a_1	6	4	70·97	71·10	71·110	0		
		4	70·81	70·95	70·933	4	Fe	
a_4	1	4	70·62	70·76	70·770	1N*d* ?	Zr, Mn	
		0	70·44	70·58	70·584	2	Ti	
	2	2	70·31	70·45	70·468	2	Co	
a_4		3	70·18	70·32	70·330	0N		(2).
		1	70·02	70·16	70·173	00		(1).
a_4	2	4	69·78	69·92	69·932	0		
a_4	4	3	69·38	69·52	69·506	0N		
		1	69·17	69·31				
a_4	4	3	69·03	69·17	69·190	0		
	2	3	68·65	68·79	68·793	00		
b_1		1	68·53	68·67	68·680	00		(1).
	0	2	68·36	68·50	68·496	000		
		2	68·18	68·32	68·319	1	Mn	
	2	2*d* ?	67·87	68·01	68·029	2	Ti, Ni, Fe	
		1	67·67	67·81	67·812	0		(1).
		1	67·49	67·63				
b_1		2	67·38	67·52	67·527	0000		
		1	67·18	67·32	67·297	1	Fe ?	
		2	66·47	66·61	66·594	000		
b_1		2	66·36	66·50	66·494	000		
		0	65·96	66·10				
b_1	00	2	65·46	65·60	65·581	0		(1).
b_2	1	1	64·93	65·07	65·081	0000		
		2	64·73	64·87	64·832	00		Corrected solar λ = 64·870.
b_1	00	4	64·66	64·80	[64·786]	00		Solar line added from HIGGS.
	1	3	64·38	64·52	64·535	0N*d* ?		
b_2		1	64·26	64·40	64·408	1	Co	
b_1	1	5*d* ?	63·95	64·09	64·055	0		Solar line wide enough to include ammonia.
b_2	0	3	63·61	63·75	63·750	1	Ni	
b_1	1	6	63·32	63·46	63·442*	0*d* ?	Co	*
					63·298	0000N		

* From 3363·4 to 3358·0 the solar lines are tabulated in full.

TABLE V.—Catalogue of Ammonia Band Lines, with Solar Comparisons (continued).

Ammonia.					Sun.			Remarks.
Series.	Intensity.		Wave-length.		λ Rowland.	Intensity.	Origin.	
	Flame.	Arc.	I.A.	Rowland.				
b_2	00	3	3362·97	3363·11	3363·107	0		
b_1	2	6	62·76	62·90	62·936	4N*d* ?	Co	
					62·782	1		
					62·727	0000		
b_2		2	62·38	62·52	62·528	0		
b_1	3	6	62·26	62·40	62·402	2*d* ?		(1).
					62·275	1		
					62·087	2	Ti	
b_1, b_2	6	8	61·84	61·98	61·988	0		
					61·906	1		
					61·704	3N*d* ?	Co	
b_1	1	4	61·47	61·61				Solar line merged in dark ground.
		4	61·42	61·56	61·568	0N		
					61·421	2		
b_1	4	4	61·16	61·30	61·327	8	Ti	
		4	61·10	61·24	61·241	1		(2).
		3	60·98	61 12	61·141	0		
b_1		4	60·90	61·04	61·055	1	Ti	
		3	60·80	60·94	60·988	0		Corrected solar λ = 60·942.
b_1	3	3	60·68	60·82	60·828	0		Dark ground, both in sun and ammonia.
		3	60·58	60·72	60·741	0		
b_1		5	60·48	60·62	60·631	0		
					60·485	1	Cr	
b_1	10	8	60·31	60·45	60·444	2	Ni	Ni not given by EXNER and HASCHEK.
b_1, c_1		3	60·19	60·33	60·345	0		Dark ground, both in sun and ammonia.
b_1		5	60·10	60·24	60·258	0		
b_1		10*d* ?	60·04	60·18	60·181	2		
c_1		4	59·94	60·08	60·066	0		
c_2 ?		5	59·75	59·89	59·936	1N		Solar line wide enough to include ammonia.
					59·823	2		
c_1		3	59·63	59·77	59·769	1		(1).
	4	5	59·50	59·64	59·636	2	Fe ?	
c_2		3	59·41	59·55	59·542	1		(2).
c_1		5	59·28	59·42	59·420	1	Co	
c_3		1	59·15	59·29				
c_2		3	59·08	59·22	59·248	3N	Ni	Not Ni in ammonia arc.
		3	59·02	59·16	59·144	00		
c_1	3	3	58·89	59·03	59·035	2N		(1).
c_3		1	58·80	58·94	58·929	00		(2).
c_2		4	58·70	58·84	58·832	0		
		2	58·65	58·79	58·771	00		(2).
c_1	4	3	58·48	58·62	58·649	4	Ti, Cr	
c_3		2	58·42	58·56	58·542	00		(2).
c_2		4	58·28	58·42	58·416	3	Ti	
					58·276	0000		

TABLE V.—Catalogue of Ammonia Band Lines, with Solar Comparisons (continued).

Ammonia.					Sun.			Remarks.
Series.	Intensity.		Wave-length.		λ ROWLAND.	Intensity.	Origin.	
	Flame.	Arc.	I.A.	ROWLAND.				
c_1, δ?	5	4	3358·04	3358·18	3358·182	IN		
					58·076*	0000		*
	5	3	57·72	57·86	57·874	0		
c_1		0	57·56	57·70	57·703	0		(1).
	5	3	57·28	57·42	57·412	2	Zr	
	4	2	56·66	56·80	56·821	2	Fe	
	2	1	55·18	55·32	55·363	4	Fe	
	1		53·91	54·05	54·057	000N		
δ	6	2	53·63	53·77	53·768	00N	Zr	
	0	1	53·10	53·24	53·262	2		(1).
	1		51·77	51·91				
ϵ	3	1	50·85	50·99	50·985	000		
		0	49·85	49·99				
δ	10	4	49·55	49·69	49·695	00		
δ'	0	0	48·68	48·82	48·820	000		
	0	0	47·94	48·08	48·072	3	Fe	
ϵ	4	2	47·62	47·76	47·760	00N		
ζ	3	0	46·42	46·56	46·557	0		(1).
		2	46·28	46·42	46·414	00		
δ	8	4	45·62	45·76	45·761	00		
δ'	0	1	44·86	45·00	45·015	000		
ϵ	5	2	44·17	44·31	44·315	00		
ζ	4	1	43·21	43·35	43·366	0		(1).
	1	1	43·01	43·15	43·156	00		
	0	1	42·33	42·47	42·442	3	Fe	
δ	8	4	41·82	41·96	41·967	4	Ti	
δ'	00		41·15	41·29	41·300	0000N		
ϵ	6	2	40·68	40·82	40·823	00N		
ζ	6	3	39·86	40·00	40·011	1		(1).
	0	?	39·30	39·44	39·438	000N		Possibly obscured in arc by "ghost."
	0	0	38·80	38·94	38·944	0000		
δ	8	4	38·10	38·24	38·247	0		
		1	37·67	37·81	37·803	3	Fe	
ϵ	6	4	37·19	37·33	37·319	1N	Co	
		1	36·75	36·89				Possibly obscured in sun by Mg 36·820 (8N).
ζ	6	2	36·49	36·63	36·635	00N		
δ	7	4	34·47	34·61	34·613	0		
ϵ	7	4	33·72	33·86	33·854	0		
		2	33·40	33·54	33·526	2	Co	
ζ	7	3	33·11	33·25	33·250	0		
		1	33·05	33·19				
δ	7	5	30·90	31·04	31·056	1N		
		1	30·59	30·73	30·745	000	Sn ?	
ϵ	7	5	30·27	30·41	30·438	1		
ζ	6	4	29·75	29·89	29·902	00		
		1	28·19	28·33	28·341	00	Co	

* From 3363·4 to 3358·0 the solar lines are tabulated in full.

TABLE V.—Catalogue of Ammonia Band Lines, with Solar Comparisons (continued).

Ammonia.					Sun.			Remarks.
Series.	Intensity.		Wave-length.		λ Rowland.	Intensity.	Origin.	
	Flame.	Arc.	I.A.	Rowland.				
δ	6	5	3327·40	3327·54	3327·533	2	Ni	
ε	5	4	26·87	27·01	26·998	3	Ti	
ζ	5	4	26·41	26·55	26·553	0		
δ	5	5	23·98	24·12	24·129	0		
ε	5	4	23·53	23·67	23·669	0		
ζ	5	4	23·12	23·26	23·256	00		
δ	4	4	20·63	20·77	20·783	2	Mn, Fe	
ε	4	3 ?	20·25	20·39	20·391	7	Ni	Obscured in arc by Ni.
ζ	4	3	19·89	20·03	20·032	0		
δ	3	3	17·37	17·51	17·514	0		
ε	3	3	17·04	17·18	17·174	00		
ζ	3	3	16·73	16·87	16·871	00		
δ	3	3	14·18	14·32	14·334	0	Mn	
ε	3	3	13·90	14·04	14·042	00N		
ζ	3	3	13·63	13·77	13·774	1		(1).
δ	3	3	11·09	11·23	11·238	0		
ε	3	3	10·85	10·99	10·996	0		
ζ	3	3	10·62	10·76	10·777	1N		(1).
δ	3	3	08·10	08·24	08·239	0N		
ε		3 ?	07·90	08·04	08·035	00N		Obscured in arc by Cu.
ζ	2	2	07·70	07·84	07·845	4	Fe	
δ	2	2	05·21	05·35	05·354	000		
ε		2	05·05	05·19	05·194	000		
ζ	2	2	04·87	05·01	05·001	00	Mn	
δ	2	2	02·42	02·56				Obscured in sun by Na 02·510 (6).
ε		2	02·30	02·44	02·443	0000N		
ζ	1	1	02·15	02·29	02·289	0000N		
δ	2	2	3299·76	3299·90	3299·905	0		(1).
ε		2	99·67	99·81	99·804	0		(1).
ζ		1	99·54	99·68	99·652	0N*d* ?	Mn	
δ	2	1	97·23	97·37	97·381	0		(1).
ε		1	97·16	97·30	97·301	0	Co	
ζ		0	97·05	97·19	97·194	0N		(1).
δ	1	1	94·82	94·96	94·949	00N		Just resolvable in 4th order plate.
ε		1	94·79	94·93				
ζ		0	94·70	94·84	94·849	000		
δ, ε	1	1	92·58	92·72	92·728	4	Fe	
ζ		0	92·51	92·65	92·636	0		(1).
δ, ε	0	1	90·50	90·64	90·642	0N		(1).
ζ		0	90·45	90·59	90·602	00		
δ, ε	0	1	88·57	88·71	88·705	2	Ti	
δ, ε		0	86·84	86·98	86·980	0N		(1).

Description of Plate.

Fig. I. is enlarged from a photograph of the spectrum of the flame of ammonia fed with oxygen; taken with a small quartz spectrograph. The bright band on the left is due to water vapour.

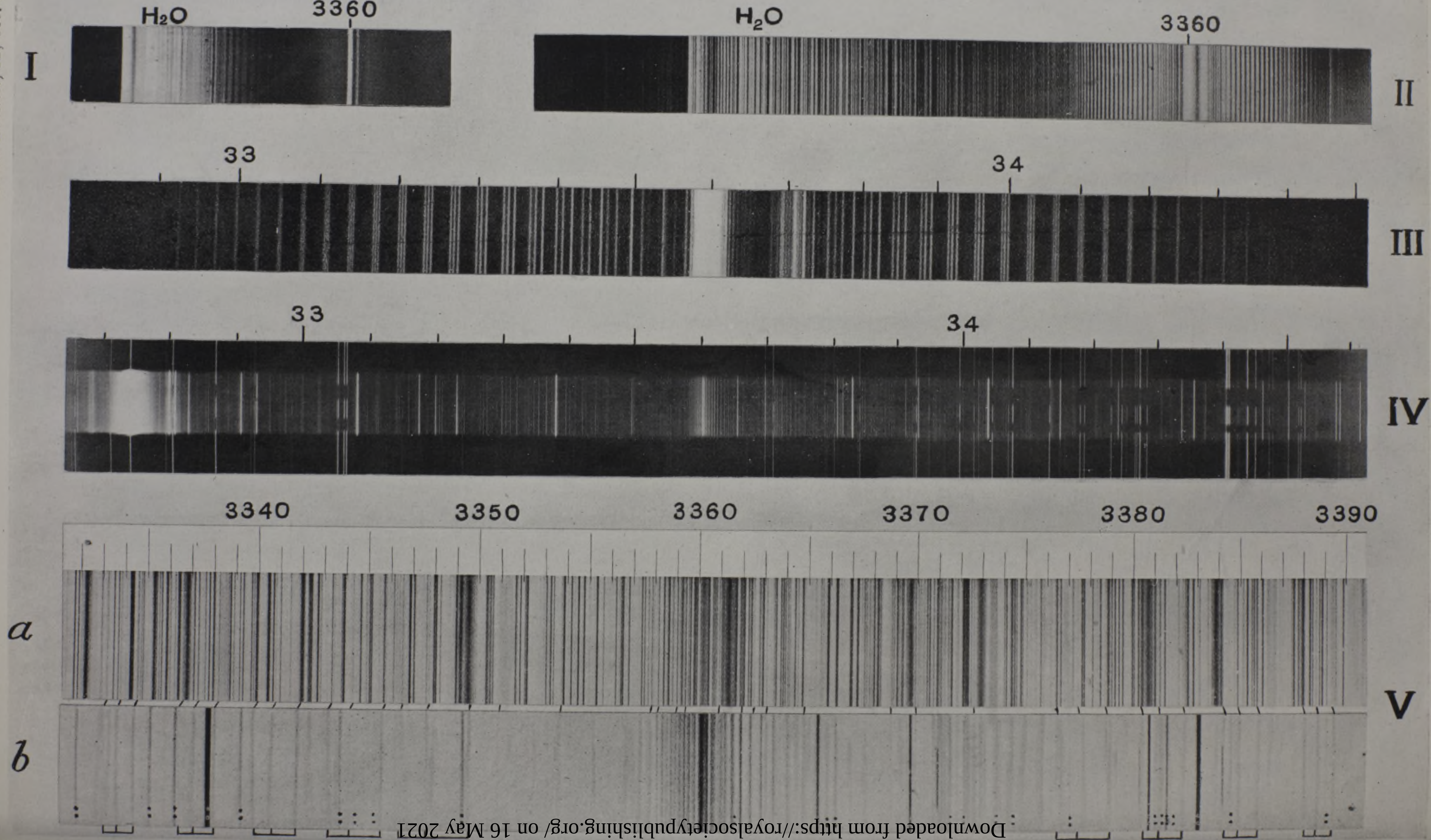
Fig. II. is from a photograph taken with a quartz spectrograph of moderate dispersion, the source being a flame of imperfectly dried cyanogen burning in an atmosphere of oxygen. The bright band on the left is due to water vapour.

Fig. III. shows the band of the ammonia flame as photographed with the large quartz spectrograph.

Fig. IV. is from a photograph taken in the 3rd order of a 10-foot concave grating. The short lines at the edges are those of the iron comparisons. The middle spectrum is that of the copper arc in ammonia.

Fig. V. (*a*) is the solar spectrum, from a photograph by Higgs; (*b*) is the copper arc in ammonia, as fig. IV. It is shown as a negative to facilitate comparison with the solar absorption lines. Metallic lines are marked by double dots, except in the case of iron comparison lines, which are short lines along the middle of the spectrum. The scale is that of Rowland. (There is a slight difference of scale of the two enlargements, but several lines common to the two spectra are indicated.)

THE AMMONIA BAND, λ 3360



PHILOSOPHICAL TRANSACTIONS.

I. BAKERIAN LECTURE.—*The Spectrum of Silicon at Successive Stages of Ionisation.*

By A. FOWLER, *F.R.S., Yarrow Research Professor of the Royal Society, Imperial College, South Kensington.*

(Lecture delivered May 15, 1924.—MS. received December 23, 1924.)

[PLATES 1—3.]

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I. INTRODUCTORY.

The spectrum of silicon has been the subject of numerous investigations, of which a convenient summary to the year 1912 has been given by KAYSER.* The spectrum is of special interest on account of the remarkable series of variations which accompany changes in the experimental conditions. These changes were first systematically investigated by LOCKYER,† who further showed that the different groups of lines which were developed with increasing intensity of discharge appeared in the spectra of stars following each other in order of increasing temperature.‡ Four distinct groups of lines were recognised by LOCKYER, namely:—

Group I.	..	λλ 3905 ·8, 4103 ·2
Group II.	..	λλ 3853 ·9, 3856 ·1, 3862 ·7, 4128 ·1, 4131 ·1, 5042, 5057.
Group III.	..	λλ 4552 ·8, 4568 ·0, 4574 ·9.
Group IV.	..	λλ 4089 ·1, 4116 ·4.§

The lines of Group I correspond to the arc spectrum, and are most strongly developed in stars approximating to the solar or G type. The chief lines of Group II are produced in the ordinary spark spectrum, but the fainter lines are best obtained in vacuum tubes; they have their greatest relative importance in stars of types F and A. Lines of Groups III and IV are also most effectively observed in vacuum tubes, and are produced in turn as the energy of the discharge is increased; they occur in successively higher stages of the stellar sequence, those of Group IV not appearing until the hotter B stars are reached.

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* 'Handbuch der Spectroscopie,' vol. 6, p. 478.

† 'Roy. Soc. Proc.,' vol. 65, p. 449 (1899); vol. 67, p. 403 (1901); vol. 74, p. 296 (1904).

‡ See also "Catalogue of 470 of the Brighter Stars," 'Solar Physics Committee' (1902).

§ *Note.*—Another line at λ 4097, at first included in this group, was afterwards shown by LUNT to be due to an impurity, and was subsequently identified by LOCKYER, BAXANDALL, and BUTLER as an enhanced line of nitrogen. ('Roy. Soc. Proc.,' A, vol. 82, p. 532 (1909)).

Lockyer's grouping of the lines was confirmed by Lunt,[*] who made an extensive series of experiments, mainly on the chloride and fluoride of silicon. These observations, however, like those of Lockyer, only extended over the comparatively small part of the spectrum which can be photographed in the stars with ordinary photographic plates.

A valuable investigation of the spectra of the chloride and fluoride of silicon was afterwards made by Porlezza,[†] covering the region λ 6371 to λ 3146. Several previously unrecorded lines were noted, especially in the region between λ 5200 and λ 5900, but no attempt was made to classify the lines in the different groups, and the wave-lengths do not appear to be of a high order of accuracy.

An account of the spark spectrum of pure elementary silicon, over the range λ 6371 to λ 2124, was given by Crookes[‡] in 1914, and the spark spectrum in the region λ 2124 to λ 1842 was observed a little later by McLennan and Edwards.[§]

Many lines not recorded by previous observers were noted by Sawyer and Paton[||] in the spectrum of a powerful " vacuum spark " discharge. These observations covered the region λ 6700 to λ 2100, but the resolution was not great and the wave-lengths were only considered to be correct within one or two-tenths of an angstrom. No attempt was made to classify the lines, but all the more important lines are included among those previously observed in the preparation of the present paper.[¶]

For completeness, it may be added that accurate determinations of the wave-lengths of nine silicon lines, which are of importance in connection with the observation of stellar radial velocities, have been made by H. Barrell in connection with the present series of observations.[**]

A comparison of the various records shows considerable divergencies in the wave-lengths assigned to the same lines, and even the silicon origin of some of the lines has remained in doubt. There has also been no systematic study of the different groups of silicon lines over a wide range of spectrum such as is required in the investigation of spectral series. It, therefore, seemed desirable to make a more exhaustive investigation of the spectrum under different conditions, with a view to obtaining the wave-lengths of the lines with greater precision and especially of obtaining the complete spectra represented by the different groups of LOCKYER. In this way it was hoped to obtain data which might lead to the identification of the series which characterise the different groups, and thence to a more complete physical explanation of the changes observed in the laboratory and in the stars.

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[*] 'Roy. Soc. Proc.,' vol. 65, p. 448 (1899); vol. 66, p. 44 (1899); A, vol. 76, p. 118 (1905); 'Annals of the Cape Observatory,' vol. 10, Part II. (1905).

[†] 'Gaz. Chim. Ital.,' vol. 42, Part 2, p. 42 (1912).

[‡] 'Roy. Soc. Proc.,' A, vol. 90, p. 572 (1914).

[§] 'Phil. Mag.,' Ser. 6, vol. 30, p. 482 (1915).

[||] 'Astrophys. Jour.,' vol. 57, p. 279 (1923).

[¶] Important observations in the extreme ultra-violet have been made by Bowen and Millikan ('Physical Review,' vol. 23, p. 1 (1924)) and by McLennan and Shaver ('Trans. Roy. Soc. Canada,' vol. 18, p. 1 (1924)). These have confirmed the existence of several lines of the fourth spectrum of silicon previously predicted by the author's observations, as indicated in Table 13. McLennan and Shaver have also observed the arc spectrum in the region λ 6320 to λ 11231.

[**] 'Monthly Notices, R.A.S.,' vol. 83, p. 322 (1923).

The investigation has been in progress during several years, and suggestive results with regard to the series were early obtained.* Publication of details, however, was long delayed by the necessity of extending the observations into the Schumann region, in which it appeared that some of the more important lines for completely establishing the various series might be expected to occur. With the aid of a grant from the Government Grant Committee of the Royal Society a suitable instrument was obtained, after much unavoidable delay, and some of the desired observations were made.

The new observations revealed many lines in addition to those previously known, in all parts of the spectrum, and numerous series have been fully or partially established for the different groups of lines. In accordance with BOHR's theory, it results that the classification of silicon lines which was first deduced by LOCKYER, from the behaviour of the lines in the laboratory and stellar spectra, has a true physical basis, and that the successive groups represent successive stages of ionisation of the silicon atoms. This conclusion depends upon the evaluation of the series constant for the series lines of different groups.

On the nucleus theory of the atom, BOHR showed how the RYDBERG series constant could be derived theoretically for hydrogen, and indicated in a general way why the same constant should appear in the formulæ for other spectra. The theory also gave an entirely satisfactory explanation of the change from the ordinary to the enhanced spectrum in the case of helium, and in the Bakerian Lecture for 1914† it was shown by the present writer that a similar explanation was applicable to other elements. It appeared from these investigations that in passing from arc to spark lines, the series were of generally similar character, but that the series constant was changed from RYDBERG's R to 4 R.‡ In other words, the enhanced lines are produced by atoms which have lost an electron or have become ionised.

The theory further indicated the possible production of other series for which the constant would have the values 9 R, 16 R, and so on, if sufficient stimulus could be applied to remove additional electrons. The work of LOCKYER strongly suggested that examples of such new types of series might be found in a further study of the varying spectrum of silicon, as has proved to be the case. In the arc spectrum, the typical series appear to be very feebly developed, and the terms have not yet been fully determined, but the investigation has definitely proved that the series corresponding with the second, third and fourth silicon groups are characterised by the respective series constants 4 R, 9 R and 16 R. The four groups of LOCKYER are therefore to be interpreted as follows :—

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* A. FOWLER. "Report on Series in Line Spectra." 'Physical Society,' p. 164 (1922).

† 'Phil. Trans.,' A, vol. 214, p. 225 (1914).

‡ In former papers the series constant was indicated by N, but in agreement with certain other workers, R will be adopted for this constant in the present paper.

Group I.—Si I, or Si = neutral atoms.
Group II.—Si II, or Si^+ = singly-ionised atoms.
Group III.—Si III, or Si^{++} = doubly-ionised atoms.
Group IV.—Si IV, or Si^{+++} = trebly-ionised atoms.

The series systems consist alternately of triplets and doublets in accordance with the so-called spectroscopic "displacement law" of KOSSEL and SOMMERFELD.

While the present work has been in progress, a similar investigation of the successive spectra of aluminium, designated Al I, Al II, and Al III, has been made by PASCHEN.[*] Sodium, magnesium, aluminium and silicon have consecutive atomic numbers, and instructive comparisons may therefore be made of the spectra of Na I, Mg II, Al III and Si IV; of Mg I, Al II and Si III; and of Al I and Si II.

The chief results with regard to the series of Si IV have already been presented to the Society,[†] but some additional data have since become available. Detailed results relating to all the lines observed at the four stages of excitation are given in the present paper, and comparisons are made with the corresponding spectra of other elements which immediately precede silicon in the periodic table. A comprehensive catalogue of the lines observed at different stages is also included; this may be expected to be of further use in connection with the observation of other spectra produced by strong discharges in vacuum tubes, since, under such conditions, silicon lines frequently appear in consequence of the decomposition of the glass.

II. OBSERVATIONAL DATA.

The Instruments Employed.

Numerous spectrographs were employed in the course of the investigation, some for preliminary observations over a large range, and others, of high dispersion, for the final determinations of wave-lengths. For measurements of the brighter lines in the visible region a 10-feet concave grating was used, chiefly in the first order, and the same instrument was used for selected regions in the ultra-violet, including λ 2218 to λ 2058. For most of the wave-length determinations in the ultra-violet as far as λ 2250, photographs were taken with a large quartz spectrograph of the Littrow type, constructed by Adam

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[*] 'Ann. d. Phys.,' vol. 71, p. 142 (1923) [Al III.]; 'Ann. d. Phys.,' vol. 71, p. 537 (1923) [Al II.].

[†] 'Roy. Soc. Proc.,' A, vol. 103, p. 413 (1923).

Hilger, Ltd. The definition given by this instrument is extremely good, and the large scale does not involve unduly long exposures. The linear dispersion ranges from 12 A per mm. at λ 4000 to 4 ·5 A per mm. at λ 3000, and 2 A per mm. at λ 2300. A small quartz spectrograph by Bellingham and Stanley was used for the determination of the wave-lengths of lines between λ 2000 and λ 1841, the dispersion at λ 1900 being about 5 ·5 A per mm.*

The wave-lengths were interpolated in the usual manner with reference to standard lines of iron. So far as possible, the values for the standards were taken from the list adopted by the International Astronomical Union,† or from the well-known table by BURNS. Between λ 2374 and λ 2290 KAYSER's wave-lengths of iron lines, corrected to the International scale, were adopted as standards, and for the region beyond λ 2290, lines of aluminium and copper given by EDER.‡

Much labour has been expended in the effort to obtain wave-lengths of a high degree of accuracy. Those obtained with the grating are distinguished in the tables by being expressed to three decimal places, and are unlikely to be more than 0 ·01 A in error. The values determined with the large quartz spectrograph are probably less accurate, but the errors should not often exceed 0 ·02 A ; the large inclination of the photographic plate in this instrument, combined with want of perfect flatness of the plates, is probably responsible for the want of closer agreement in the values obtained from different photographs.

For the calculation of wave-numbers, the wave-lengths were corrected to vacuum by the tables published by the Washington Bureau of Standards.§

The Vacuum Spectrograph.

The vacuum spectrograph utilized for observations in the extreme ultra-violet was constructed by Adam Hilger, Ltd. It is provided with a 4-inch concave grating having a radius of 1 metre and 15,000 lines per inch. The grating was specially ruled at the Johns Hopkins University with a view to its use for the extreme ultra-violet, and has been found quite satisfactory for observations down to about λ 800. The wave-lengths from different plates, however, are less consistent than might have been expected, probably on account of irregularities in the sensitive films of the plates employed. The instrument has so far been mainly used with a fluorite window covering the slit, in order that vacuum tubes of silicon fluoride and sparks in hydrogen at atmospheric pressure might be used as sources. The region covered by the present observations has thus been mainly restricted to wave-lengths on the less refrangible side of λ 1250. The dispersion in the first order spectrum is 17 ·2 A per millimetre. Suitable standards were provided by LYMAN's wave-lengths of aluminium lines, and by SIMEON's wave-lengths of carbon lines.* The adopted values for the silicon lines are probably correct within one- or two-tenths of an angstrom.

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* The author is indebted to the Government Grant Committee of the Royal Society for this instrument.

† 'Trans. Int. Ast. Union,' vol. 1, p. 41 (1922).

‡ 'Zeit. f. Wiss. Phot.,' vol. 14, p. 137 (1915).

§ 'Scientific Papers,' No. 327 (1918).

The author is indebted to Mr. F. SIMEON, of the research laboratory of Adam Hilger, Ltd., for placing at his disposal an excellent photograph of the silicon vacuum arc covering the region λ 1405–λ 990. This has provided a useful check on the author's observations in the common region, and some additional data in the region more refrangible than λ 1250. Some of the lines in this region have also been measured by BOWEN and MILLIKAN,† and the mean of SIMEON's and MILLIKAN's wave-lengths for one of the lines, 997·70, has been taken as a standard in the author's measurements, the other standard being the hydrogen line λ 1215·68.

The Arc Spectrum.

As a check on previous records of the arc spectrum by ROWLAND and others, photographs were taken of the spectrum of pure silica and of potassium fluosilicate when introduced into the carbon arc, and of the arc between pieces of fused silicon. With silica on poles of Acheson graphite the impurities were very slight, but with fused silicon lines of iron and other elements were sometimes numerous, especially in the ultra-violet. The lines which it is believed may certainly be attributed to silicon are those indicated as lines of Si I in Tables X and XII.

All the lines tabulated by ROWLAND‡ were observed, together with a few others, including some prominent lines in the ultra-violet which were outside the range of ROWLAND's observations.

It is of interest to note that three of the previously unrecorded arc lines of silicon have been found to correspond with three unidentified solar lines tabulated by ROWLAND, namely :—

Silicon Arc.	Sun.	
λ I. A.	λ ROWLAND.	Intensity.
5797·855	5798·077	3
5793·070	5793·292	3
5780·378	5780·600	0

Besides the lines of Group I, EXNER and HASCHEK have included the red pair of Group II (λλ 6371, 6347) as appearing faintly in the arc spectrum. As in the case of magnesium, and many other elements, however, these spark lines are restricted to a region very close to the poles of the arc. This method of producing the red pair was, in fact, employed by the author in 1906, in the identification of the red pair of lines in the solar and chromospheric spectra.§

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[*] 'Roy. Soc. Proc.,' A, vol. 102, p. 484 (1922); vol. 104, p. 368 (1923).

[†] 'Physical Review,' vol. 23, p. 1 (1924).

[‡] "New Table of Standard Wave-lengths," *Astronomy and Astrophysics*, vol. 12, p. 321 (1893).

[§] 'Monthly Notices, R.A.S.,' vol. 67, p. 157 (1906).

In the far ultra-violet, the silicon arc also shows a number of well-marked flutings, which were first recorded by DE GRAMONT and DE WATTEVILLE.* These flutings have also been observed under other conditions, and it would appear that they have been correctly attributed to the oxide of silicon.†

The Spark Spectrum.

For observations of the spark spectrum the ordinary condensed discharge from a 12-inch induction coil was passed between poles of fused silicon.

All the brighter arc lines in the ultra-violet appear in this spectrum, as do also the brighter lines of Si II. Many of the fainter lines of Si II which appear in vacuum tubes, however, do not certainly occur in the spark, probably because under these conditions they are very diffuse as well as faint. Some of the brighter lines of Si III are also present, and even the brighter lines of Si IV may be found in the regions near the electrodes, as was also noted by LUNT and by LOCKYER, BAXANDALL and BUTLER. Photographs of the spark in an atmosphere of hydrogen, which were especially necessary in observations in the Schumann region, showed an increased development of lines belonging to Si III and Si IV; the comparison of sparks with and without self-induction was of great assistance in distinguishing lines of different classes.

The silicon lines attributed to Si II are collected in Tables X and XIII. It is to be understood that only the more prominent of these are observed in the ordinary spark spectrum, and that they are accompanied by the brighter lines of Si I and Si III.

The "spark" spectrum was further studied by observations of the arc between poles of fused silicon *in vacuo*. Under these conditions the chief lines of Si II were well developed, and occurred with perfect sharpness, so that wave-lengths could be determined with a high order of accuracy.

Two lines given by CROOKES as occurring in the spark spectrum at λ 3438·300 and λ 3247·551 (I.A.) have not been recorded by any other observer, and have not been confirmed; the second line is very close to the strong copper line 3247·53.

Several of the lines at first included by EXNER and HASCHEK as belonging to the silicon spark have already been shown to be due to impurities by EBERHARD and LUNT, namely, 4103·7, 4030·1, 4021·0, 3883·46 and 3853·62. In addition, lines given by EXNER and HASCHEK at 2446·63 and 2443·91 have not been observed.

The original table of spark lines given by EDER and VALENTA (as quoted in KAYSER'S 'Spectroscopie,' vol. 6, p. 490) includes several faint lines which have also not been traced in the present series of observations; these are not in the list given by EDER and VALENTA in their well-known 'Atlas of Spectra,' and are probably due to impurities.

As a general remark, it may be noted that the spark does not provide so useful a means of investigating the lines of Si II as is provided by observations of silicon compounds in vacuum tubes.

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* 'Comptes Rendus,' vol. 147, p. 239 (1908).

† See also W. JEVONS: 'Roy. Soc. Proc.,' vol. 106, p. 174 (1924).

Vacuum Tube Spectra.

For observations of vacuum tube spectra the tubes were filled with the vapour of silicon chloride, or with silicon tetrafluoride, and subjected at various pressures to induction-coil discharges of varying intensity. In agreement with the observations previously made by LUNT,[*] it was found that lines of the higher silicon groups were more satisfactorily obtained from the tetrafluoride than from the chloride, and most of the observations were, therefore, made on the tetrafluoride.

The capillary tubes used were observed "end-on" through quartz windows, thus permitting photographs to be taken in the ultra violet. For the special development of lines of Si II it was found advantageous to use rather wide tubes, ranging up to 1·5 mm. internal diameter. For Si IV tubes of internal diameter 1 mm. or less gave the best results. For work with the vacuum spectrograph the discharge tube was provided with a fluorite window, which was sealed on the slit plate.

Silicon chloride obtained commercially was found to be of a high degree of purity, so that when care was taken to exclude atmospheric gases the only lines which could not be assigned to silicon or chlorine were a few lines due to carbon.

In the earlier experiments silicon tetrafluoride was prepared by the action of sulphuric acid on a mixture of calcium fluoride and silica. Later, on the suggestion of Prof. SMITHELLS, it was found more convenient to prepare the gas by heating barium fluosilicate. Before passing to the discharge tube the gas traversed a tube containing phosphorus pentoxide, in order to remove water vapour, and before reaching the pump it successively passed over potash and phosphorus pentoxide. The latter arrangement effectively prevented the gas entering the pump, provided that the exhaustion was not too rapid. To reduce inevitable carbon impurities, all stopcocks were lubricated as sparingly as possible with tap grease. It was found convenient to have a large bulb immediately following the hard glass generating tube, for the purpose of storing a quantity of the gas at nearly atmospheric pressure. Small quantities were then admitted to the discharge tube, as required, by the usual arrangement of a short length of tube between two taps. This small compartment was necessary for the readjustment of the pressure, especially during the passage of strong discharges. A barometer tube on the high-pressure side of the apparatus, which could be shut off at will by means of a stopcock, was useful as a safety valve and pressure indicator.

With ordinary precautions there was no difficulty in obtaining the gas with the requisite purity, except for carbon impurities, which appear to be almost unavoidable, and sometimes chlorine. The degree of purity and the character of the spectrum under the action of any particular discharge could usually be sufficiently judged by visual observations, but when using the vacuum spectrograph, photographs in the ultra-violet were also frequently taken through a second quartz window to indicate more surely the stage of ionisation which had been reached.

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[*] 'Roy. Soc. Proc.,' A, vol. 76, p. 118 (1905).

The uncondensed discharge through silicon tetrafluoride is of a deep blue colour, and the predominant feature is a group of bands in the region λ 4200 — λ 4500, due to the undissociated gas; bands are also numerous from about λ 3100 to λ 2300, and the brighter lines of Si I also appear. The bands do not appear in the capillary when condensed discharges are employed, but they often appear in the photographs of end-on tubes on account of the discharge in the wider portions. By appropriate adjustment of the condenser and air-gap, it was easy to obtain the equivalent of the ordinary spark spectrum, showing the lines of Si II at maximum intensity and much sharper than in the spark. Increased intensity of discharge gives a special development of lines of Si III; and, finally, by considerably reducing the pressure of the gas, the lines of Si IV may be obtained with maximum intensity. It should be observed, however, that lines of Si IV and Si III nearly always appear together. Examples of the photographs, with full descriptions, are given later.

Photographs were also taken of the spectra given by strong discharges through highly exhausted glass or quartz tubes, the tubes being originally filled with helium or oxygen. Under these conditions, the lines of Si IV were obtained with their greatest intensity. The silicon lines could be identified by their coincidences with the lines obtained in other ways, and by comparison with the spectrum of oxygen which was under investigation in the laboratory at the same time; the silicon lines were also distinguishable by their restriction to a comparatively small part of the width of the spectrum, while the oxygen lines extended completely across the spectrum. In these tubes many of the arc lines were suppressed, or nearly so, and lines of Group II considerably reduced in relative intensity. These observations provided the most trustworthy means of distinguishing the lines of silicon from those due to fluorine.

The same phenomena were observed with tubes of glass, but in that case it was observed, in accordance with the previous observations of Lunt, that lines of calcium, sodium and other elements were also obtained.

All the lines catalogued by Lunt and by Porlezza between the red and λ 3190 appear on the present series of photographs (with the exception of a faint line at 3191 ·15), together with many additional lines.

III. Theoretical Predictions and Nomenclature.

The Series Constant.

In order to avoid repetition, it will be convenient to refer next to the theoretical predictions as to the character of the spectra which may be expected to appear at successive stages of ionisation.

Bohr's theoretical formula for the series constant may be written

$$C = \frac{2\pi^2 e^2 m}{ch^3} \frac{M}{M+m} (ne)^2$$

where e and m respectively indicate the charge and mass of the electron, M the mass of the nucleus of the atom, c the velocity of light, h PLANCK's constant, and ne the net charge of the "core," or rest of the atom, with respect to the "series electron" which generates the spectrum by its quantum changes of orbit.

In the case of arc spectra, n has unit value and the series constant, apart from the term correcting for the mass of the nucleus, is equal to the hydrogen constant R. The factor $M/(M+m)$ differs very little from unity and has only a small influence on the series constant. The so-called spark spectrum is produced when the exciting agency is sufficiently powerful to remove one of the electrons out of the range of effective action of the nucleus. The atom is then ionised, and the spectrum is produced by one of the next outermost electrons. This interacts with the remainder of the atom, which now has a net positive charge $2e$, and the series constant becomes 4R. This predicted change, as previously mentioned, was verified by the author in the Bakerian Lecture of 1914. The theory further indicated that atoms which have lost two electrons, or have become doubly ionised, would be found to be characterised by series involving the constant 9 R, and so on. The theoretical prediction has now been verified in the case of silicon so far as trebly-ionised atoms, which have 16R for the series constant. The degree of ionisation is, in fact, most surely indicated by the value of the corresponding constant for the series.

Alternating Types of Series.

The theory further indicates that the spectra obtained at successive stages of ionisation should vary in type. The familiar arc series of sodium, magnesium and aluminium, together with the author's previous work on the spark spectrum of magnesium, and PASCHEN's work on ionised aluminium* provide material for a nearly complete comparison with the four spectra of silicon. The relations to be expected may be shown as follows :—

	Group I. Doublets.	Group II. Triplets.	Group III. Doublets.	Group IV. Triplets.
$n = 1$ C = R	Na I 11 +, 10 −	Mg I 12 +, 11 −	Al I 13 +, 12 −	Si I 14 +, 13 −
$n = 2$ C = 4R	Mg II 12 +, 10 −	Al II 13 +, 11 −	Si II 14 +, 12 −	
n = 3 C = 9R	Al III 13 +, 10 −	Si III 14 +, 11 −		
$n = 4$ C = 16R	Si IV 14 +, 10 −			

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[*] *Loc. cit.*

Under each symbol the number preceding the + sign represents the nuclear charge, and that preceding the — sign the number of external electrons apart from that which generates the spectrum, so that in the first row the atoms as a whole are neutral. The atomic numbers of Na, Mg, Al and Si are respectively 11, 12, 13, 14, and the neutral atoms give spectra consisting alternately of doublets and triplets.* The spectrum of neutral silicon (Si I) includes triplets and, as shown in the table, the spectrum of ionised silicon (Si II) may be expected to be similar to that of neutral aluminium (Al I) and to yield a system of doublets. In the same way, the spectra of Si III and Si IV were expected to resemble in type the spectra of Mg I and Na I respectively. All spectra in the same vertical column of the foregoing table should, in fact, be of the same type. Corresponding lines in the spectra, however, would be expected to be displaced to shorter wave-lengths as the degree of ionisation is increased, in consequence of the increased nuclear charge. These predictions have also been realised, as will presently appear.

Series Notation.

The series notation adopted in the present paper is mainly that of the author's "Report on Series," in which singlet terms are represented by mS, mP, mD, mF, doublets by $m\sigma$, $m\pi$, $m\delta$, $m\phi$, and triplets by ms, mp, md, and mf. In accordance with more recent usage, however, the multiple doublet and triplet terms have been modified as follows :—

Doublets.		*Triplets.*	
Old	New	Old	New.
δ'	δ_2	d'', d', d	d_3, d_2, d_1
δ	δ_1	f'', f', f	f_3, f_2, f_1

The nomenclature of the diffuse and fundamental terms is thus brought into accordance with that of the principal terms.

It is now recognized that there is no limit to the number of possible types of terms, and a nomenclature for types additional to the four earliest known has become necessary. The more familiar terms are characterized by azimuthal quantum numbers (k)† as follows :—

s, S or σ terms	$k = 1$
p, P or π ,,	$k = 2$
d, D, or δ ,,	$k = 3$
f, F, or ϕ ,,	$k = 4$

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* Recent investigations of the more complex spectra of elements of the higher groups have shown that this sequence takes the form of alternate even and odd multiplicities. The maximum multiplicity increases by unity in successive groups, and is one greater than the number of the group in the periodic table. In Group I the maximum multiplicity is 2, in Group II it is 3, and the spectra are correspondingly simple. (See *e.g.*, A. LANDÉ, Zeit. f. Phys., vol. 15, p. 189 (1923).) This extended view of multiplicities, however, scarcely enters into the discussion of the spectra dealt with in the present communication, as the quintet terms expected in Si I appear to be absent or very feebly developed.

† Sommerfeld : 'Atomic Structure and Spectral Lines,' English edition, p. 365.

It is clear according to the general theory that there may be other types for which the characteristic azimuthal quantum numbers are higher than 4. In ordinary arc spectra, series involving such terms occur in the infra-red, and their true character has only been revealed through the occurrence of similar series in the ordinary region of observation in the spectra of ionised elements. Ionised magnesium, for example, includes a series which was approximately represented by $3\phi - m\phi$,* but the $m\phi$ terms were afterwards recognized by Bohr and others as a new set of terms, designated $m\phi'$, which differ but little from the $m\phi$ terms and approach still more closely to the terms of hydrogen.† In Al III and Si IV, this fifth set of terms combines with another set $m\phi''$ to produce a sixth type of series. The fifth and sixth series have been called by Paschen the Super-Bergmann ("Über-Bergmann") and Super-super-Bergmann ("Über-über-Bergmann") series respectively. Similar series in a triplet system would be designated f' and f''; ϕ' and f' are characterized by the azimuthal quantum number 5, and ϕ'', f'' by the number 6.

It would clearly have been inconvenient to adopt this notation permanently, and g has been substituted for f' by several workers. This modification has also been made in the present paper, and in view of the convenience of retaining the Greek letters for doublets the sixth series of terms will be indicated by k for triplet terms and κ for doublet terms. Thus:

Old Notation.	New Notation.	Az. Quant. No.
f', F$'$, or ϕ'	g, G or γ	5
f'', F$''$, or ϕ''	k, K, or κ	6

The symbol used for a term will ordinarily give a sufficient indication of the associated azimuthal quantum number.

Numeration of Series Terms.

The values of the principal quantum numbers assigned to the various spectral terms by Bohr‡ are very different from the numbers of Rydberg or Ritz, and the ordinary series formulæ do not indicate them. On the new system groups of electrons in the normal atom, such as were previously considered to be arranged in rings about the nucleus, are assigned principal quantum numbers increasing outwards, the first (K) group having the quantum number 1, the second (L) group 2, and so on. The second ring or group is completed at neon (atomic number 10), and in the normal states of the atoms of elements having atomic numbers from 11 to 18 (argon) the outer electrons (M group) occupy orbits having the principal quantum number 3. The azimuthal quantum numbers associated with the normal states are indicated by the highest terms of the spectral series in accordance with the previous remarks; for example, if the highest term be $2p$, a 2_2 orbit is indicated for the series electron. For circular orbits n and k are equal, and the greater the difference between n and k the greater will be the eccentricity of the orbit.

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* A. Fowler: 'Phil. Trans.,' A, vol. 214, p. 253 (1914).

† 'Roy. Soc. Proc.,' A, vol. 103, p. 419 (1923).

‡ 'Ann. d. Phys.,' vol. 71, p. 260 (1923).

While Bohr's new system of numeration is of undoubted importance in theoretical discussions, it would seem to be more convenient to retain the older numbers for descriptive purposes. These have the advantage of being identical for corresponding lines in the spectra of different elements of the same group, and also of being directly related to the formulæ which are in general use for the approximate representation of series. Comparison with existing compilations of spectroscopic data will also be facilitated thereby.

In the present paper the Rydberg-Hicks numeration will be adopted, as in the author's "Report on Series," but so far as possible an indication will be given of the alterations necessary for reduction to the Bohr system. In general, but not invariably, the number assigned to a term on the Rydberg-Hicks system is the integral part of $\sqrt{\mathrm{R}/\mathrm{term}}$, *i.e.*, the integral part of the "effective quantum number."

The following comparison of the different systems of numeration as applied to the first terms of sodium, magnesium, and aluminium may be useful for reference.

	Rydberg.			Ritz-Paschen.			Bohr.		
	Na	Mg	Al	Na	Mg	Al	Na	Mg	Al
Singlets		1 S			1 S			3 S	
		1 P			2 P			3 P	
		2 D			3 D			3 D	
		3 F			4 F			4 F	
Doublets	1 σ		2 σ*	1 *s*		2 *s*	3 *s*		4 *s*
	1 π		1 π	2 *p*		2 *p*	3 *p*		3 *p*
	2 δ		2 δ	3 *d*		3 *d*	3 *d*		3 *d*
	3 φ		3 φ	4 *f*		4 *f*	4 *f*		4 *f*
Triplets		2 *s**			2 *s*			4 *s*	
		1 *p*			2 *p*			3 *p*	
		2 *d*			3 *d*			3 *d*	
		3 *f*			4 *f*			4 *f*	

* These are designated 1 σ and 1 *s* in the author's "Report on Series," but the original numeration of Rydberg is more appropriate, it being then supposed that the 1 *s* term does not occur.

Inner Quantum Numbers.

In the consideration of some of the groups of lines which occur in the spectra of silicon, it becomes necessary to refer to the so-called "inner quantum numbers" (j) which have been assigned to the various types of spectral terms by Sommerfeld and Landé.[*] For the purposes of the present paper it will suffice to note the following :—

	Singlets.				Doublets.					Triplets.						
Terms	S	P	D	F	σ	π_1	π_2	δ_1	δ_2	s	p_1	p_2	p_3	d_1	d_2	d_3
j	0	1	2	3	1	2	1	3	2	1	2	1	0	3	2	1

Ordinary terms combine with each other in accordance with the selection rule $\Delta j = \pm 1$ or 0, except that the transition 0 to 0 does not occur. Combinations are further subject to the selection rule for azimuthal quantum numbers, $\Delta k = \pm 1$.

There is another class of terms, usually designated p', d', etc., which do not form part of the regular sequences, and are possibly due to the simultaneous transitions of two electrons with the emission of a single quantum of energy.[†] These are subject to the selection rule for inner quantum numbers, but the ordinary azimuthal quantum condition for their combination with the regular terms appears to be replaced by $\Delta k = 0$.[‡]

IV. Regularities in the Spectrum of Si I.

General Features of the Spectrum.

In the region extending from the red about λ 6700 to the ultra-violet at λ 2000 the arc spectrum of silicon includes 45 lines, of which only 13 occur in the visible spectrum, and only four in the region between λ 3900 and λ 2640. Several of the lines in the ultra-violet are of great intensity, but in the visible spectrum the lines are relatively weak. Several of the ultra-violet lines are easily reversed in the arc.

A comparison of the arc and spark spectra shows that enhanced lines do not appear at all in the arc, except in the region close to the poles when elementary silicon is employed, and all the lines which appear in the middle of an ordinary arc have accordingly been assigned to Si I. The wave-lengths, intensities, and wave-numbers of the lines between λ 6700 and λ 2000 are collected in Table X and of those between λ 2000 and λ 1840 in Table XII.

The complete series arrangement of the lines of Si I has not yet been traced, but it seems sufficiently clear that the main features arise from triplet and singlet terms. The triplet series, however, are but feebly represented, and as the first members occur far in the ultra-violet, succeeding members would only be expected as weak lines in the early Schumann region.

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[*] 'Zeit. f. Phys.,' vol. 15, p. 189 (1923).

[†] See 'Roy. Soc. Proc.,' A, vol. 107, p. 39 (1925).

[‡] Laporte : 'Zeit. f. Phys.,' vol. 26, p. 16 (1924).

Triplets of Si I.

A triplet of the sharp series and another of the diffuse series are unmistakable, namely :—

Sharp Triplet.

λ, Int.	ν	Δν
2452·136 (3)	40768·42	
		146·12
2443·378 (3)	40914·54	
		77·10
2438·782 (3)	40991·64	

Diffuse Triplet.

λ, Int.	ν	Δν	
2218·917 (1)	45052·96		
		17·00	
2218·080 (2)	45069·96		
		28·36	
2216·165 (4)	45098·32		
			146·03
2211·750 (2)	45198·92		
		17·15	
2210·912 (3)	45216·07		
			77·17
2207·980 (2)	45276·09		

A careful search has been made for other triplets, but with no certain results. There are, however, three lines with apparently the same separations forming part of an isolated group of five lines beginning at λ 1881·6.[*] Details of these lines are as follows :—

λ, Int.	ν	Δν
1880·71 (1)	53171	
		147
1875·54 (2)	53318	
		76
1872·87 (2)	53394	

The first line, however, which would be expected to be the strongest in a regular series, is definitely the weakest of the three, and the agreement in separations is possibly accidental. If regarded as the second $p\ s$ triplet, the value of p given by a Rydberg formula would be about 64100.

Apart from this, there are no direct means for the determination of even the approximate limits of the triplet series.[†] There are also no arc lines in the less refrangible part of the spectrum which seem at all likely to represent an associated

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[*] The possibility of these lines forming a triplet was first suggested to the author by Prof. McLennan.

[†] *Note.*—When the lecture was delivered, a limit of 85000 was considered to be a probable value for the triplet series, on the ground that in most of the known series of triplets the limit is rather more than double the wave-number of the first sharp triplet. It has since been noticed, however, that in most series the ratio of the limit to the first sharp triplet tends to diminish as the wave-number of the triplet increases, and the estimate was probably too high.

"principal" series ($2s - mp$), and no suitable representatives of a fundamental series ($2d - mf$), having separations $\Delta d_{21} = 28$ and $\Delta d_{32} = 17$. In view of the feeble development of the triplets themselves, it would seem that these series do not occur with sufficient intensity to appear in the present records of the spectrum.

Multiplets of Si I.

Some of the most intense lines of the arc spectrum are included in the well-known characteristic group of six lines extending from λ 2506 to λ 2528, all of which are reversed in the arc. These form a pp' multiplet, involving the triplet separations noted above, and it follows that the first terms of the combinations which give rise to the lines must be $1p_1$, $1p_2$ and $1p_3$. The group may be represented schematically as below, where numbers in brackets following the wave-numbers represent intensities and the inner quantum numbers (j) are indicated by numbers beneath or alongside the term symbols :

p_1		p_2		p_3		
(2)		(1)		(0)		j
		39605·89 (8)			p'_3	(0)
		77·14				
39537·01 (9)	*146·02*	39683·03 (7)	*77·01*	39760·04 (7)	p'_2	(1)
194·72		*194·80*				
39731·73 (10)	*146·10*	39877·83 (9)			p'_1	(2)

A prominent group of lines beginning with λ 1988 also consists of six strong lines and may be represented in a similar manner ; namely

p_1		p_2		p_3		
(2)		(1)		(0)		j
50277·3 (4R)	*146·3*	50423·6 (3)			p''_1	(2)
66·8		*67·2*				
50344·1 (2)	*146·7*	50490·8 (2)	*77·1*	50567·9 (3)	p''_2	(1)
		35·9				
		50526·7 (2)			p''_3	(0)

The wave-numbers in this group are subject to a little uncertainty, mainly for lack of good standards of reference, but it is evident that the combinations involve the regular p terms and another set of terms of similar type represented by p''. It will be observed that the latter terms are in reverse order in this multiplet, the largest term being p''_1.

All the terms entering into the above multiplets clearly belong to triplet systems. No multiplets involving quintet terms, such as might have been expected from the sequence of multiplicities to which reference has previously been made have yet been identified.

It may be further remarked that, although the actual values of the various p terms cannot yet be stated, their differences are known with considerable accuracy. In particular, it will be useful to note the difference $1p'_2 - 1s$:

$$\left.\begin{array}{ll} 1p_1 - 1s & = 40768\cdot42 \\ 1p_1 - 1p'_2 & = 39537\cdot01 \end{array}\right\} 1p'_2 - 1s = 1231\cdot41$$

$$\left.\begin{array}{ll} 1p_2 - 1s & = 40914\cdot54 \\ 1p_2 - 1p'_2 & = 39683\cdot03 \end{array}\right\} 1p'_2 - 1s = 1231\cdot51$$

$$\left.\begin{array}{ll} 1p_3 - 1s & = 40991\cdot64 \\ 1p_3 - 1p'_2 & = 39760\cdot04 \end{array}\right\} 1p'_2 - 1s = 1231\cdot60$$

$$\text{Mean, } 1p'_2 - 1s = 1231\cdot51$$

The Singlet Series of Si I.

Six of the stronger singlets, all of which can be obtained as reversed lines in the arc, can be arranged in two series, which are apparently to be identified as the sharp and diffuse series. A fourth line of the sharp series is suggested by the greater intensity of the more refrangible component of a pair of Si II lines, λλ 1817, 1808, in a photograph of the silicon spark in hydrogen with large self-induction. This is near the expected position of the next member of the sharp series and has been regarded as such.

The data and formula for the sharp series, as calculated from the last three lines, are as follows :—

λ, Int.	ν
2881 ·585 (10R)	34692 ·97
2124 ·140 (6R)	47062 ·94
1901 ·00 (5R)	52603 ·9
1808 ·14	55305

$$\left.\right\}\begin{array}{l} 1\text{P} = 60072 \\ m\text{S} = \text{R}\Big/\left(m + 0\cdot689685 + \dfrac{0\cdot427838}{m}\right)^2. \end{array}$$

The correcting term is unusually large, but, notwithstanding this, the extrapolated wave-number for the first line only differs by 919 from the observed value. If calculated from the first three lines, $1p = 60020$.

The data and formula for the diffuse series are :—

λ, Int.	ν
2435·159 (8R)	41052·61
2058·20 (5R)	48570·51
1893·02 (2R)	52832

$$1\mathrm{P} = 59339{\cdot}0$$

$$m\mathrm{D} = \mathrm{R}\Big/\left(m + 0{\cdot}933784 + \frac{0{\cdot}515257}{m}\right)^2.$$

The correcting term is again exceptionally large, so that neither of the series closely follows a Rydberg formula. The two values for 1P also differ more than usual, but as the sharp series is generally more accurately represented than the diffuse, the value from the sharp series has been adopted ; namely, 1P = 60072.

With this limit, the terms and effective quantum numbers are :—

Terms.	$\sqrt{\mathrm{R/Term}}$.	Terms.	$\sqrt{\mathrm{R/Term}}$.
1S = 25379·03	2·078837	1D = 19019·39	2·401387
2S = 13009·06	2·903604	2D = 11502·49	3·087909
3S = 7468·1	3·832263	3D = 7240·2	3·892110
4S = 4767	4·796648		

The increase in the successive effective quantum numbers departs much more from unity than in most of the known series, but the fact that all the lines are readily reversed in the arc is strongly in favour of the above arrangement, in which the largest term is 1P.

Other Regularities in Si I.

A remarkable feature of the silicon arc spectrum is the occurrence of the separation $1p'_2 - 1s$ in connection with some of the strong singlets, including the line which has been designated 1P — 1S. Thus :—

$$\left.\begin{array}{l} 25597{\cdot}61\ (9) - 24365{\cdot}89\ (5) = 1231{\cdot}72 \\ 34692{\cdot}97\ (10) - 33461{\cdot}39\ (5) = 1231{\cdot}58 \end{array}\right\} = 1p'_2 - 1s.$$

These separations may be considered to be equal within the limits of observational errors, and their significance seems to be assured by the fact that the lines in question are strong and well separated from neighbouring lines. Further combinations between triplet and singlet terms are suggested by the following lines :—

ν — ν — Δν

$17645{\cdot}64\ (1) - 17568{\cdot}52\ (2) = 77{\cdot}12 = 1p'_3 - 1p'_2 = 1p_3 - 1p_2$

$17707{\cdot}97\ (2) - 17513{\cdot}19\ (5) = 194{\cdot}78 = 1p'_2 - 1p'_1$

$33656{\cdot}27\ (1) - 33461{\cdot}39\ (5) = 194{\cdot}88 = 1p'_2 - 1p'_1$

The line 33461, it should be noted, has already been included in the above consideration of the separation $1p'_2 - 1s$.

Much time has been expended in attempting to trace the connection between the triplet and singlet systems, but no satisfactory conclusions have yet been reached. There are sufficient indications, however, that the highest term will be found to be a P or a p term, and since the principal quantum number must be 3, it is probable that the series electron normally occupies a 3_2 orbit.

As the term $1p$ has not yet been determined, the first ionisation potential of silicon cannot be stated. The value of the term 1P, however, indicates that the ionisation potential cannot be less than 7·5 volts.

V. THE DOUBLET SERIES OF Si II (Si^+).

General Remarks.

The spectrum of Si II forms a doublet system, some of the leading members of which have long been familiar from their occurrence in the ordinary spark spectrum.

From the beginning of the research it seemed sufficiently obvious by inspection that the red pair at λλ 6371, 6347, the yellow pair at λλ 5979, 5958, and the green pair at λλ 5056, 5041, were respectively the first members of principal, sharp and diffuse series, having a wave-number separation approximating to 60. Other members of the series, however, long eluded detection, and it now appears that the difficulty was due to the very rapid fall of intensity in passing along the respective series. This is especially the case in the principal series, where even the second member is very faint notwithstanding the great brightness of the pair in the red. One additional pair was found in the observations of silicon chloride, but the most complete representation of the doublets was obtained in the experiments on silicon tetrafluoride. In the latter case the lines appear as well-isolated pairs with appropriate separation, and there can be no doubt as to their association with the red, yellow, and green pairs. It is easily shown from the numerical data that the ordinary series constant is not applicable to these lines, and that a number of the order of 4R is required. The hydrogen value of 4R (= 438713·2) has accordingly been adopted in the calculation of formulæ for these series.

The series $1\pi_{12} - m\sigma$ and $2\pi_{12} - m\sigma$ have been distinguished as the "first sharp" and "second sharp" series respectively; and similarly for the diffuse series. As in Al I, there is no 1σ term in Si II.

The lines which have been identified as belonging to Si II are collected in order of wave-length in Tables X and XIII.

The experimental behaviour of the classified lines included in the table accords with their assignment to Si II. There are also many lines which would seem to belong to Si II, on experimental grounds, for which no series relations have been found. Many such lines occur in the visible part of the spectrum, and the lines λλ 4188, 4191 first observed by Lunt are noteworthy examples. In this connection it should be remembered that the spark spectrum includes lines which certainly belong to Si III, so that the occurrence of a line in the spark and not in the arc is not in itself a sure criterion for its classification as Si II. It is here that the vacuum tube spectra have the advantage, for spectra can be produced in which lines of Si II occur with great intensity, while lines of Si III are faint or absent.

The Series System of Si II.

The consistency of the allocations of the lines composing the Si II system of series is clearly shown by calculating formulæ for the separate series.

The Principal Series.—Three pairs of lines are available for the calculation of the limit of the principal series. The wave-numbers of the stronger components of the pairs and the formula derived from them are as follows :—

$$\left.\begin{array}{l} 2\sigma - 2\pi_1 = 15750 \cdot 90 \\ 2\sigma - 3\pi_1 = 38384 \cdot 52 \\ 2\sigma - 4\pi_1 = 48562 \cdot 70 \end{array}\right\} \quad \nu = 66297 \cdot 06 - 4\mathrm{R}/(m + 1 \cdot 001375 - 0 \cdot 110567/m)^2.$$

The term $2\pi_1$ thus calculated is 50546·16 and it follows from the separation $\Delta\nu = 60$ that $2\pi_2 = 50606 \cdot 16$. These are in very satisfactory agreement with the values derived independently from the second sharp and diffuse series as indicated below.

The Second Sharp and Diffuse Series.—The sharp and diffuse series should give the same limits, apart from errors of observation and inadequacy of the type of formula employed, and these should agree with the values of 2π calculated from the principal series. The Hicks formulæ for the two series, and the data from which they were calculated, are as follows :—

$$\left.\begin{array}{l} 2\pi_2 - 3\sigma = 16780 \cdot 61 \\ 2\pi_2 - 4\sigma = 29992 \cdot 96 \\ 2\pi_2 - 5\sigma = 36772 \cdot 91 \end{array}\right\} \quad \nu = 50621 \cdot 40 - 4\mathrm{R}/(m + 0 \cdot 644962 - 0 \cdot 133206/m)^2.$$

$$\left.\begin{array}{l} 2\pi_2 - 3\delta_2 = 19831 \cdot 58 \\ 2\pi_2 - 4\delta_2 = 31203 \cdot 07 \\ 2\pi_2 - 5\delta_2 = 37330 \cdot 50 \end{array}\right\} \quad \nu = 50710 \cdot 77 - 4\mathrm{R}/(m + 0 \cdot 661311 + 0 \cdot 323876/m)^2.$$

The limits given by the Ritz formula in the form

$$\nu = \mathrm{A} - 4\mathrm{R}/[m + \mu + \alpha\,(\mathrm{A} - \nu)]^2$$

lead to the values 50638·13 and 50683·24 respectively. All are as nearly in agreement with each other, and with the value 50606·16 calculated for $2\pi_2$ above, as is to be expected.

The Fundamental Series.—This is a series of narrow doublets, $\Delta\nu = 16 \cdot 6$, having a separation equal to that of the chief line and satellite in the first member of the diffuse series. The wave-numbers of the more refrangible components and the formula calculated from them are as follows :—

$$\left.\begin{aligned} 2\delta_2 - 3\phi &= 24217 \cdot 69 \\ 2\delta_2 - 4\phi &= 34421 \cdot 75 \\ 2\delta_2 - 5\phi &= 39972 \cdot 60 \end{aligned}\right\} \quad \nu = 52483 \cdot 11 - 4\mathrm{R}/(m + 0 \cdot 894930 + 0 \cdot 134295/m)^2,$$

i.e., $2\delta_2 = 52483 \cdot 11$; $2\delta_1 = 52466 \cdot 51$; $3\phi = 28265 \cdot 42$.

These values cannot be directly compared with the terms for the other series, as the first member of the diffuse series lies in the far infra-red and has not been observed. The value of the term 3ϕ, however, may be applied in connection with certain combination series to adjust all the limits, besides leading to values for 1π.

Combination Series.—Besides the series lines so far considered, there is a well-known group of three spark lines, beginning with λ 3862, which presents the appearance of an inverted diffuse set and must therefore have negative wave-numbers assigned to it. These cannot be deduced from any of the already known terms, but may be represented by introducing new terms of diffuse type, x_1 and x_2, as shown below.

The terms x, the magnitudes of which are indicated by the previously calculated values of 2π, combine with the ϕ terms to give a strong series of fundamental type in the extreme ultra-violet, beginning with a pair at λ 2073. For greater consistency of numerical results the wave-numbers for this pair have been slightly adjusted so as to make their separation 15·91, like that of the two more accurately measured lines νν 25942, 25926, to which they are related. The observed wave-numbers 48232·89 and 48248·49 have thus been altered to 48232·74 and 48248·65. The terms x_1 and x_2 may then be calculated as follows :—

$$\begin{aligned} x_1 - 3\phi &= 48232 \cdot 74 \\ 3\phi &= 28265 \cdot 42 \\ \hline x_1 &= 76498 \cdot 16 \end{aligned} \qquad\qquad \begin{aligned} x_2 - 3\phi &= 48248 \cdot 65 \\ 3\phi &= 28265 \cdot 42 \\ \hline x_2 &= 76514 \cdot 07 \end{aligned}$$

For the calculation of $2\pi_1$ and $2\pi_2$ we have

$$\left.\begin{aligned} 2\pi_1 - x_2 &= -25942 \cdot 05 \\ 2\pi_1 - x_1 &= -25926 \cdot 14 \\ 2\pi_2 - x_2 &= -25882 \cdot 04 \end{aligned}\right\} \quad \begin{aligned} 2\pi_1 &= 50572 \cdot 02 \\ 2\pi_2 &= 50632 \cdot 03 \end{aligned}$$

The values of 2π thus obtained are very close to those calculated from the principal series and to the mean of those determined from the sharp series by the Hicks and Ritz formulæ. These values will accordingly be adopted to fix the common limits of the second sharp and diffuse series; at the same time the values above given for x_1 and x_2 are brought into accurate relationship with the other terms.

The term 2σ can at once be derived; namely,

$$\begin{aligned} 2\sigma - 2\pi_1 &= 15750 \cdot 90 \\ 2\pi_1 &= 50572 \cdot 02 \\ \hline 2\sigma &= 66322 \cdot 92 \end{aligned}$$

The First Sharp and Diffuse Series.—From general considerations, the chief lines of the Si II spectrum are to be expected in the extreme ultra-violet. In the photographs of this region there are two very striking pairs of lines, which are brought out by a moderate stimulus in silicon tetrafluoride, and which also appear in the silicon spark in hydrogen. One of these pairs, about λ 1533, has been found to be the first member of the sharp series, while the other at λλ 1817·06, 1808·14, is a combination pair involving the x terms. A third pair, at λλ 1265, 1260, which also appears strongly in the photograph taken by SIMEON, is the first member of the diffuse series. Still another pair, about the lower wave-length of SIMEON's photograph, λλ 993·1, 990·3, is the second member of the first diffuse series. The common limits of the two series have been calculated from the sharp pair, $1\pi - 2\sigma$ with the aid of the previously determined term 2σ; thus,

$$\left.\begin{aligned} 1\pi_1 - 2\sigma &= 65208 \\ 1\pi_2 - 2\sigma &= 65495 \end{aligned}\right\} \qquad \begin{aligned} 1\pi_1 &= 131531 \\ 1\pi_2 &= 131818 \end{aligned}$$

In this way all the limits required for the construction of the series table have been brought into proper relation with each other. Their general accuracy as regards the extreme ultra-violet is shown by the close agreement of the observed and calculated values for lines which have not been used in the determination of the limits.

The results of the discussion of the series of Si II are collected in Table I, which calls for little further explanation. The limits have been adopted from the calculations already given and the terms have been derived in the usual manner by subtracting the wave-numbers of observed lines from the corresponding limits. The numbers under m are those of the RYDBERG system, and the numbers (+ 2), etc., indicate the alterations to give the numbers on BOHR's new system.

Table I.—Series of Si II (Si^+).

1st Sharp Series.—$1\pi - m\sigma$; $1\pi_1 = 131531$; $1\pi_2 = 131818$.

λ, Intensity.	ν	$\Delta\nu$.	m (+ 2).	$m\sigma$.
*1533·55 (10) *1526·83 (8)	65208 65495	287	(2)	66323
(1023·75) (1020·75)	(97680) (97967)	(287)	(3)	33851
(901·78) (899·45)	(110892) (111179)	(287)	(4)	20639

Principal Series.—$2\sigma - m\pi$; $2\sigma = 66322 \cdot 92$.

λ, Intensity.	ν.	$\Delta\nu$.	m (+ 2)	$m\pi_1$, $m\pi_2$
−1533·55 (10) −1526·83 (8)	−65208 −65495	287	(1)	131531 131818
6347·091 (10) 6371·359 (8)	15750·90 15690·90	60·00	(2)	50572·02 50632·02
2604·44 (2) 2606·09 (1)	38384·52 38360·21	24·31	(3)	27938·40 27962·71
2058·53 (1) 2058·92 (0)	48562·70 48553·61	9·09	(4)	17760·2 17769·3

2nd Sharp Series.—$2\pi - m\sigma$; $2\pi_1 = 50572 \cdot 02$; $2\pi_2 = 50632 \cdot 02$.

λ, Intensity.	ν.	$\Delta\nu$.	m (+ 2)	$m\sigma$
−6347·091 (10) −6371·359 (8)	−15750·90 −15690·90	60·00	(2)	66322·92
5978·970 (5) 5957·612 (4)	16720·63 16780·61	59·98	(3)	33851·40
3339·84 (3) 3333·16 (2)	29932·98 29992·96	59·98	(4)	20639·05
2726·74 (2) 2722·29 (1)	36662·99 36722·91	59·92	(5)	13909·07

* Used for calculation of $1\pi_1$, $1\pi_2$. A line of Si IV is apparently coincident with λ 1533·5.

TABLE I (continued).

1st Diffuse Series.—$1\pi - m\delta$; $1\pi_1 = 131531$; $1\pi_2 = 131818$.

Observed.		Calculated.		Δν.	m (+ 1).	$m\,\delta_2$, $m\,\delta_1$.
λ vac., Intensity.	ν.	λ vac.	ν.			
*1265·04 (10)	79049	1265·06 1264·78	79048 79065	16·6		52483
1260·66 (8)	79324	1260·48	79335	287	(2)	52466
*†993·09 (1) †990·32 (1)	100696 100977	992·74 989·92	100731 101018	287	(3)	30800

2nd Diffuse Series.—$2\pi - m\delta$; $2\pi_1 = 50572{\cdot}02$; $2\pi_2 = 50632{\cdot}02$.

λ, Intensity.	ν.	Δν.	m (+ 1).	$m\delta_2$, $m\delta_1$.
Out of range	(−1911·09) (−1894·49) (−1851·09)	(16·60) (60·00)	(2)	52483·11 52466·51
5056·353 (2) 5055·975 (7) 5041·020 (5)	19771·60 19772·90 19831·58	1·30 59·98	(3)	30800·42 30799·12
*3210·04 (3) 3203·89 (2)	31143·30 31203·07	59·77	(4)	19428·8
*2682·27 (2) 2677·98 (1)	37270·80 37330·50	59·70	(5)	13301·4

Fundamental Series.—$2\delta - m\phi$; $2\delta_1 = 52466{\cdot}51$; $2\delta_2 = 52483{\cdot}11$.

λ, Intensity.	ν.	Δν.	m (+ 1).	$m\phi$.
4130·884 (10) 4128·053 (8)	24201·08 24217·69	16·61	(3)	28265·42
2905·70 (3) 2904·29 (2)	34405·06 34421·75	16·69	(4)	18061·40
2501·99 (1) 2500·96 (1)	39956·15 39972·60	16·45	(5)	12510·43

* Satellites not resolved.

† From Simeon's photograph.

TABLE I (continued).

Combination Series of Si II.—$x - m\phi$; $x_1 = 76498{\cdot}16$; $x_2 = 76514{\cdot}07$.

λ, Intensity.	ν.	Δν.	Calculated.
−3853·657 (3) −3856·021 (8) −3862·592 (6)	−25942·05 −25926·14 −25882·04	15·91* 60·01	$2\pi_1 - x_2$ $2\pi_1 - x_1$ $2\pi_2 - x_2$ } Used for calculation of $2\pi_1$, $2\pi_2$.
2072·61 (10) 2071·94 (8)	48232·89 48248·49	15·60	$x_1 - 3\phi$ $x_2 - 3\phi$ } Used for calculation of x_1, x_2.
(λ vac.)			
1817·06 (10)	55034	271	$\{1\pi_1 - x_2 = 55017 = \lambda\ 1817{\cdot}62$ $\{1\pi_1 - x_1 = 55033 = \lambda\ 1817{\cdot}09$
1808·14 (8)	55305		$1\pi_2 - x_2 = 55304 = \lambda\ 1808{\cdot}19$
1711·0 (6*d* ?)	58445		$\{x_1 - 4\phi = 58437 = \lambda\ 1711{\cdot}2$ $\{x_2 - 4\phi = 58453 = \lambda\ 1710{\cdot}8$
1563·1 (3*d* ?)	63975		$\{x_1 - 5\phi = 63988 = \lambda\ 1562{\cdot}8$ $\{x_2 - 5\phi = 64004 = \lambda\ 1562{\cdot}4$
1485·4 (3)	67322		$\{x_1 - 6\phi\dagger = 67329 = \lambda\ 1485{\cdot}2$ $\{x_2 - 6\phi = 67345 = \lambda\ 1484{\cdot}9$
1438·9 (1*n*)	69498		$\{x_1 - 7\phi = 69494 = \lambda\ 1439{\cdot}0$ $\{x_2 - 7\phi = 69510 = \lambda\ 1438{\cdot}6$
1408·8 (0*n*)	70982		$\{x_1 - 8\phi = 70974 = \lambda\ 1409{\cdot}0$ $\{x_2 - 8\phi = 70990 = \lambda\ 1408{\cdot}6$

* This is definitely smaller than the separation in the fundamental series (16·61).

† The formula gives $6\phi = 9169$, $7\phi = 7004$, $8\phi = 5524$.

In addition to the series shown in Table I, the "super-fundamental" series, $3\phi - m\gamma$, is possibly represented, but is somewhat doubtful, because of the absence of the first-expected member of the series. The possible second and third members are λλ5202·51, 4683·018 (νν 19216·15, 21347·79). Taking these as $3\phi - 6\gamma$ and $3\phi - 7\gamma$ respectively, with $3\phi = 28265{\cdot}42$, the resulting terms are $6\gamma = 9049{\cdot}27$ and $7\gamma = 6917{\cdot}63$. These differ from the corresponding ϕ terms in the expected direction towards $4\mathrm{R}/m^2$, but there is no line corresponding with the term 5 γ, which would be about ν 15920.

It should also be mentioned that there is a possible "multi-doublet" in the extreme ultra-violet, formed from λλ 1197·79 (3), 1194·89 (5), 1193·62 (3), and 1190·80 (4). There is at present no experimental evidence as to the class to which these lines belong, but they form an isolated group, and the occurrence of the separation 287 suggests that they may belong to Si II. The wave-numbers may be arranged as a $\pi\pi'$ combination in the following manner :—

$1\pi_1$		$1\pi_2$	
(2)		(1)	j
83487	*292*	83779	π'_2 (1)
203		*198*	
83690	*287*	83977	π'_1 (2)

The discordances between the separations, which might be expected to be equal, are within the limits of error of measurement in this region, and if the combination be significant, it results that $\pi'_1 = 47841$, $\pi'_2 = 48042$.

The highest term of Si II is a "p"-term, and on BOHR's theory the associated azimuthal or subordinate quantum number must therefore be 2. It thus appears that in the normal state of the ionised atom, and probably also in the neutral atom, the 13th electron moves in a 3_2 orbit.

The second ionisation potential of silicon, deduced from the above value of $1\pi_2$ in the usual manner, is 16·27 volts.

Comparison of Si II and Al I.

In accordance with the spectroscopic displacement law, it was to be expected that the series of Si II would be found to be generally similar to those of Al I. Both spectra are, in fact, constituted of doublets, and differ chiefly in the wider separation of the pairs in Si II, and in the displacement of lines of Si II to the region of much shorter wave-lengths as compared with corresponding lines of Al I. This, of course, is due to the greater charge of the "core," or "atomic residue," with respect to the series electron in the case of Si II as compared with that of Al I.

Comparison of Chief Lines.—Some of the corresponding lines of the two spectra are indicated in Table II.

TABLE II.—Comparison of Chief Lines of Si II and Al I.

Series.	Al I.	Si II.
	λ	λ
$1\pi_1 - 2\sigma$	3961·54	1533·55
$1\pi_2 - 2\sigma$	3944·03	1526·83
$1\pi_1 - 2\delta_2$	3092·84	—
$1\pi_1 - 2\delta_1$	3092·72	1265·04
$1\pi_2 - 2\delta_2$	3082·16	1260·66
$2\sigma - 2\pi_1$	21166	6347·09
$2\sigma - 2\pi_2$	21098	6371·36
$2\pi_1 - 3\delta_1$	16752	5056·02
$2\pi_2 - 3\delta_2$	16721	5041·06
$2\delta_1 - 3\phi$	11255	4130·88
$2\delta_2 - 3\phi$		4128·05

The table illustrates very clearly how lines of Al I which occur in the near ultra-violet are represented in Si II by lines which appear in the Schumann region, while infra-red lines of Al I correspond with lines of Si II which occur in the visible spectrum.

The main doublet separations, $1\pi_2 - 1\pi_1$, are 112 for Al I and 287 for Si II, in the ratio 1 : 2 ·56.

Effective Quantum Numbers.—The values of the terms of Al I and Si II are most effectively compared for theoretical purposes by a statement of the effective quantum numbers; that is, of the values of $\sqrt{\mathrm{R/term}}$ for Al I and of $\sqrt{\mathrm{4R/term}}$ for Si II. These are given, with the BOHR numeration of terms, in Table III.

TABLE III.—Effective Quantum Numbers of Al I and Si II.

BOHR Numbers.		3	4	5	6	7
$m\sigma$	Al I		2·186892	3·217954	4·227570	5·231357
	Si II		2·571925	3·599996	4·610472	5·616184
$m\pi_2$	Al I	1·507207	2·674639	3·700549	4·709045	
	Si II	1·824328	2·943593	3·960963	4·968841	
$m\pi_1$	Al I	1·508958	2·675967	3·701923	4·710388	
	Si II	1·826318	2·945339	3·962685	4·970115	
$m\delta_1$	Al I	2·631031	3·425462	4·260130	5·164510	
	Si II	2·891673	3·774168	4·751900	5·743038	
$m\phi$	Al I		3·968941	4·963713		
	Si II		3·939695	4·928499	5·921808	

An important difference between the two spectra is the appearance in Si II of the strong series $x - 3\phi$, which has not been found in Al I.

Comparison of Si II and C II.

Elements belonging to the same sub-group of the periodic table exhibit certain progressive spectral differences with increase of atomic weight, or of atomic number,* and it is now possible to observe such relations in the spectra of the two ionised elements, silicon and carbon, the data for C II having already been communicated to the Society.†

It may be noted in the first place that the main doublet separations for Si II and C II, which are 287 and 58 respectively, follow the usual rule that the separations are roughly proportional to the squares of the atomic numbers, their ratio being 5 ·0 as compared with 5 ·4 from the atomic numbers 28 and 12. It also appears that the two ionised elements follow the rule that the limits of the sharp and principal series (1π and 2σ, respectively) are displaced towards the red with increase of atomic number. This result is included in the general comparison of the spectral terms given in Table IV.

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* See FOWLER'S "Report on Series," p. 43.

† 'Roy. Soc. Proc.,' vol. 105, p. 299 (1924).

TABLE IV.—Spectral Terms of Si II and C II.

RYDBERG Numbers.	1	2	3	4	5
x C II		100165			
x_2 Si II		76514			
$m\sigma$ C II		80121	39425	23311	(15387)
Si II		66323	33851	20639	13909
$m\pi_2$ C II	196670	64934	34140		
Si II	131818	50632	27963	17769	
$m\delta_1$ C II		51108	28535	18164	(12558)
Si II		52466	30800	19429	13301
$m\phi$ C II			27680	17703	12283
Si II			28265	18061	12510

It should be remarked also that the corresponding δ and ϕ terms increase in passing from C II to Si II, exactly as they do with increase of atomic number in the case of the alkali metals.

Although Si II resembles C II in having a term "x," it is important to note that whereas in Si II this term is definitely of δ type, it is apparently of σ type in C II.

VI. THE TRIPLETS AND SINGLETS OF SI III (Si^{++}).

General Remarks.

The third spectrum of silicon forms a triplet system, with its accompanying series of singlets, as in the spectra of the alkaline earths. One of the triplets, having its strongest line at λ 4552, is well known from its occurrence in the spark and in certain stellar spectra. A second triplet, having its strongest line at λ 3806, is also present in the spark, but the Si III spectrum as a whole is but feebly represented under spark conditions. The lines are much more completely revealed by the vacuum tube observations of silicon fluoride, and they appear under conditions of discharge which are consistent with their assignment to doubly-ionised silicon. As in Si II, the lines which appear in the ordinary region of observation with gratings or quartz spectrographs belong to secondary series. The chief members lie in the extreme ultra-violet and have only been partially observed. The author's observations include the triplet beginning at λ 1113, and for the first two members of the triplet beginning at λ 997 he is indebted to the photograph of the silicon vacuum arc placed at his disposal by Mr. SIMEON.

The lines which have been identified as belonging to the triplet system of Si III are collected in Table V and again in order of wave-length in Tables X and XIII.

The Triplet System of Si III.

Of the four triplets which have been observed in the ordinary range, two are inverted and must therefore be given negative signs in the calculation of limits. One of them, having its strongest line at λ 3086, is accompanied by satellites, and there is accordingly no difficulty in deciding as to the two triplets which belong to the diffuse series, although the satellites to the second triplet have not been resolved. The satellites observed are abnormal, inasmuch as they appear on the more refrangible (actually less refrangible because of the inversion) side of the chief lines; in other words, $d_1 > d_2 > d_3$. The corresponding triplet in Al II, as observed by PASCHEN, is similarly inverted and has the same abnormality in connection with the satellites.

As only two members of the sharp and two of the diffuse series have been observed in the ordinary region, the data are inadequate for precise calculations of limits. The following RYDBERG formulæ, however, may be quoted as indicating the approximate limits :—

Second Diffuse series :—

$$\left.\begin{aligned} 2p_3 - 2d_3 &= -\,32282\cdot21 \\ 2p_3 - 3d_3 &= 26367\cdot96 \end{aligned}\right\} \quad \nu = 95459\cdot16 - 9\mathrm{R}/(m + 0\cdot779813)^2.$$

Second Sharp series :—

$$\left.\begin{aligned} 2p_3 - 2s &= -\,21852\cdot99 \\ 2p_3 - 3s &= 30945\cdot58 \end{aligned}\right\} \quad \nu = 96070\cdot00 - 9\mathrm{R}/(m + 0\cdot893226)^2.$$

These results are sufficient to show the order of magnitude of the term $2p_3$, and in view of the approximate character of the formulæ, the accordance of the two calculated limits provisionally serves to justify the assumption that the series constant for these triplets is 9R.

Taking $2p_3 = 96070$, and assuming the usual RYDBERG relations, the formulæ lead to λ 1340 as the approximate position of the leading triplet of the first diffuse series. The earlier photographs with the vacuum spectrograph, taken through a fluorite window, showed no such triplet in the region less refrangible than λ 1220, but later photographs of the vacuum arc, taken without window, revealed it at λ 1113. This triplet is more strongly shown in SIMEON's photograph and has also been recorded by MILLIKAN.

The triplet of the first sharp series has only been partially recorded. Its position with respect to the first diffuse triplet is accurately known from the fact that the interval separating the two is identical with that separating the triplets at λ 4552 and λ 3086. The triplet lies beyond the region photographed by the author, but the first two members appear near the limit of sensitivity on SIMEON's plate.

With the term $2d$ roughly determined from the above formulæ, and by assuming a value for the first f term, which is nearly the same for most series, it seemed probable that the first member of the fundamental series must be the complex line about λ 1500. It then became clear that a narrow triplet beginning at λ 4829 must belong to the fg, or super-fundamental, series and that a fainter triplet having its first line at λ 3040 was the second member of this series.

The last-named triplets appear to provide the most suitable means of fixing the limits of the various series. Not more than two members of any of the series have so far been observed, and the g terms may be expected to show the least departure from simple Rydberg terms. We thus have

$$\left.\begin{aligned} 3f_1 - 4g &= 20702\cdot79 \\ 3f_1 - 5g &= 32875\cdot14 \end{aligned}\right\} \quad \begin{aligned} 3f_1 &= 60444\cdot00 \\ 3f_2 &= 60483\cdot44 \\ 3f_3 &= 60511\cdot23 \end{aligned}$$

In view of the triple character of the f terms, as well as of the d terms, the line of the fundamental series near λ 1500 is a complex of six components. Owing to the small resolving power of the vacuum spectrograph, however, only three components have been observed. It may be supposed that one of these represents $2d_1 - 3f_1$, and the d_2 and d_3 terms may then be deduced by using the values of $\Delta\nu$ from the diffuse triplet at λ 3086. Thus :—

$$\begin{aligned} 2d_1 - 3f_1 &= 66649 \\ 3f_1 &= 60444 \end{aligned} \qquad \begin{aligned} 2d_1 &= 127093\cdot00 \\ 2d_2 &= 127090\cdot86 \\ 2d_3 &= 127088\cdot85 \end{aligned}$$

The possible df combinations may be most clearly indicated by making use of the inner quantum numbers (j), to which reference has already been made. Under ordinary conditions the permissible combinations are those of terms for which the values of j differ by unity or zero, with the exception that transitions $j = 0$ to $j' = 0$ do not usually occur. The df combinations are, therefore, as follow :—

Values of j.

$$d_1f_1 = d_3 - f_4 = 66649\cdot00 \qquad \text{(adapted to agree with observation).}$$

$$\left.\begin{aligned} d_1f_2 &= d_3 - f_3 = 66609\cdot56 \\ d_2f_2 &= d_2 - f_3 = 66607\cdot42 \end{aligned}\right\} \quad \text{observed} = 66608.$$

$$\left.\begin{aligned} d_1f_3 &= d_3 - f_2 = 66581\cdot77 \\ d_2f_3 &= d_2 - f_2 = 66579\cdot63 \\ d_3f_3 &= d_1 - f_2 = 66577\cdot62 \end{aligned}\right\} \quad \text{observed} = 66578.$$

The values of the $2d$ terms above determined immediately lead to the terms $2p$ and $3d$, through the observed lines of the second diffuse series, and $2p$ then gives the values of the s terms with the aid of the observed lines of the second sharp series. The terms $2p$ thus arrived at are in sufficient agreement with the approximate values previously calculated independently from the second sharp and diffuse series. The chief remaining terms, $1p$, have been derived from the first diffuse triplet at λ 1113. All the results for the triplet system which are at present available are collected in Table V.

TABLE V.—Triplet Series of Si III.

1st Sharp Series.—$1p - ms$; $1p_1 = 216879$; $1p_2 = 217142$; $1p_3 = 217273$.

Observed.			Calculated.			m (+ 2).	ms
λ.	ν.	Δν.	λ.	ν.	Δν.		
997·70	100230	249	997·81	100219	263	(2)	116660
995·23	100479		995·20	100482	131		
—	—	—	993·91	100613			

1st Diffuse Series.—$1p - md$; $1p_1 = 216879$; $1p_2 = 217142$; $1p_3 = 217273$.

Observed.			Calculated.	m (+ 1).	md_1 d_2 d_3
λ.	ν.	Δν.			
1113·76	89786	266	Used for calculation of $1p$.	(2)	127093
1110·47	90052	132			127091
1108·85	90184				127089

Fundamental Series.—$2d - mf$; $2d_1 = 127093{\cdot}00$; $2d_2 = 127090{\cdot}86$; $2d_3 = 127088{\cdot}85$.

Observed.			Calculated.			m (+ 1)	mf_1 f_2 f_3
λ.	ν.	Δν.	λ.	ν.	Comb.		
1500·39	66649	41	*1500·39	*66649·00	d_1f_1	(3)	60444·00 60483·44 60511·23
1501·32	66608	30	1501·29	66609·56	d_1f_2		
			1501·34	66607·42	d_2f_2		
			1501·91	66581·77	d_1f_3		
1502·00	66578		1501·96	66579·63	d_2f_3		
			1502·01	66577·62	d_3f_3		
1142·74 ?	87509	161			d_1f_1	(4)	39584 ? 39744 ?
1144·85 ?	87348				$d_{21}f_2$		
—	—				—		—

* Used for calculation of $2d_1$.

TABLE V (continued).

Principal Series.—$2s - mp$; $2s = 116659·56$.

λ, Intensity.	ν.	Δ ν.	m (+ 2).	$mp_1\ p_2\ p_3$.
—997·70 —995·23 —	—100230 —100479 —(100613)	249 (134)	(1)	216890 217139 217273
4552·654 (9) 4567·872 (7) 4574·777 (4)	21959·17 21886·01 21852·99	73·16 33·02	(2)	94700·39 94773·55 94806·57

2nd Sharp Series.—$2p - ms$; $2p_1 = 94700·33$; $2p_2 = 94773·54$; $2p_3 = 94806·64$.

λ, Intensity.	ν.	Δ ν.	m (+ 2).	ms.
—4552·654 (9) —4567·872 (7) —4574·777 (4)	—21959·17 —21886·01 —21852·99	73·16 33·02	(2)	116659·56
3241·67 (6) 3234·00 (5) 3230·55 (3)	30839·43 30912·57 30945·58	73·14 33·01	(3)	63861·01

2nd Diffuse Series.—$2p - md$; $2p_1 = 94700·33$; $2p_2 = 94773·54$; $2p_3 = 94806·64$.

λ, Intensity.	ν.	Δ ν.	m (+ 1).	$md_1\ d_2\ d_3$.
—3086·225 (7) —3086·429 (3) —3086·620 (0) —3093·423 (6) —3093·613 (3) —3096·786 (4)	—32392·67 —32390·53 —32388·51 —32317·31 —32315·31 —32282·21	2·14 2·02 73·21 2·00 33·10	(2)	127093·00 127090·86 127088·85
3806·56 (5) 3796·11 (4) 3791·41 (3)	26263·00 26335·30 26367·96	72·30 32·66	(3)	68438·08

$1S - 1p_2 = 39330$ $1S = 256472.$

TABLE V (continued).

Super-Fundamental Series.—$3f - mg$; $3f_1 = 60444{\cdot}00$; $3f_2 = 60483{\cdot}44$; $3f_3 = 60511{\cdot}23$.

λ, Intensity.	ν.	Δ ν.	m (+ 1).	mg.
4828·923 (4n) 4819·740 (3n) 4813·290 (2n)	20702·79 20742·23 20770·02	39·44 27·79	(4)	39741·21
3040·93 (1) 3037·26 (1) 3034·74 (1)	32875·14 32914·87 32942·20	39·73 27·33	(5)	27568·82

Six lines forming a pp' multiplet may be arranged as follows :—

$1p_1$		$1p_2$		$1p_3$	
(2)		(1)		(0)	j
		76,845			p'_3 (0)
		131			
76,712	*264*	76,976	*133*	77,109	p'_2 (1)
264		*263*			
76,976	*263*	77,239			p'_1 (2)

$p'_1 = 139{,}903$; $p'_2 = 140{,}166$; $p'_3 = 140{,}297$

This group is well defined and confirms very closely the values of the main triplet separations already adopted. A similar multiplet appears in Al II, with its first line at λ 1767·6 (ν = 56574), and in Mg I with the first line at λ 2783 (ν = 35922).

The highest term of the triplet series is a p term, but a still higher term is to be expected in connection with the associated singlets, so that the p term in question gives no direct indication of the normal state of the doubly-ionised silicon atom.

Comparison of Triplets of Si III, Al II, and Mg I.

In accordance with the normal atomic numbers of the three elements a close similarity between the spectra of Si III, Al II and Mg I is to be expected. All three spectra do, in fact, include triplet systems in association with singlets. The three atoms in the states indicated by the symbols have the same number of external electrons, but the nuclei differ in mass and charge. The effect of mass is so small as to be negligible in the present discussion, but, as previously explained, the effect of increased nuclear charge is to displace the spectrum as a whole to the region of short wave-lengths.

Corresponding Lines.—Some of the chief corresponding lines of the triplet systems are indicated in Table VI.

TABLE VI.—Comparison of Chief Lines of Si III, Al II and Mg I.

——		Mg I.	Al II.	Si III.
1st sharp, $1p_1 - 2s$	λ	5183	1862	998
	ν	19286	53692	100230
2nd sharp, $2s - 2p_1$	λ	—	7042	4553
	ν	—	14196	21959
1st diffuse, $1p_1 - 2d_1$	λ	3838	1725	1114
	ν	26046	57970	89786
2nd diffuse, $2d_1 - 2p_1$ . . .	λ	—	10080	3086
	ν	—	9921	32393
Fundamental, $2d_1 - 3f_1$. . .	λ	14877	3587	1500
	ν	6720	27874	66649

The Triplet Separations.—Increase of nuclear charge in similarly constituted atoms results in increased separations of the components of the triplets as shown in Table VII.

TABLE VII.—Triplet Separations of Si III, Al II and Mg I.

——	Mg I.	Al II.	Si III.
At. Wt.	24·32	27·1	28·3
Nuclear charge	12	13	14
Charge of core (c)	1	2	3
Separations Δp_{21}	40·9	125·5	263
Separations Δp_{32}	19·9	61·8	131

A striking result of the comparison is that the ratio of the two separations of the respective triplets is practically constant and equal to 2 : 1. Further, there is a nearly linear relation between the separations and the squares of the residual charges. Thus, the equation

$$\Delta\nu = 13 + 28c^2$$

gives the values 41, 125, 265 for Mg I, Al II and Si III respectively, and it may be observed that there is an uncertainty of a few units in the tabulated value for Si III, as it depends upon measurements in the extreme ultra-violet. The separations are, therefore, much more simply related than those of successive elements belonging to the same group of the periodic table. This has also been noted in the previous paper on Si IV.

Effective Quantum Numbers.—In the comparison of the effective quantum numbers of Si III, Al II and Mg I (Table VIII), the numbers represent $\sqrt{9R/\text{term}}$, $\sqrt{4R/\text{term}}$ and $\sqrt{R/\text{term}}$ respectively. For Al II the value of R has been taken as 109734·98 as adopted by Paschen for this spectrum. For the other elements R = 109678·3.

Table VIII.—Effective Quantum Numbers of Si III, Al II, and Mg I.

Bohr numbers.		3.	4.	5.	6.
ms	Mg I		2·314482	3·345514	
	Al II		2·691566	3·716978	
	Si III		2·908850	3·931549	
mp_1	Mg I	1·660865	2·817126		
	Al II	1·959816	3·075940		
	Si III	2·133402	3·228536		
md_1	Mg I	2·827920	3·829341		
	Al II	2·791874	3·801090		
	Si III	2·786896	3·797805		
mf_1	Mg I		3·959795	4·953992	
	Al II		3·928628	4·882470	
	Si III		4·041150	4·993692 ?	
mg	Mg I			—	—
	Al II			4·982972	5·980675
	Si III			4·983806	5·983737

The Singlets of Si III.

There are numerous lines which are developed in the silicon spectrum simultaneously, or nearly so, with the triplets of Si III, and many of them doubtless belong to the associated singlet system. The arrangement of these in series has not yet been finally accomplished, and may not be possible until improved observations in the region beyond λ 1200 have been obtained. The identification of the resonance line, 1S — $1p_2$, and of the first line of the principal series, 1S — 1P, however, can be made with reasonable certainty.

Considerable assistance might be expected from comparisons with the singlet series of Mg I and Al II. Those of Mg I are well known, but those of Al II are unfortunately not yet fully established. Paschen has not published any singlet series for Al II, but H. N. Russell[*] has attempted to trace the leading members of the four series from

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[*] 'Nature,' vol. 113, p. 163 (1924).

Paschen's data. Russell's method was to form ratios of corresponding s, p, d terms of Al II and Mg I, and to plot these ratios against the known terms of Mg I. Then, from the known S, P, D terms of Mg I the ratio of the singlet terms of Al II and Mg I were obtained by interpolation. The rough values of the singlet terms thus obtained suggested the allocation of some of the lines of Al II.

Only two members of each of the triplet series have been observed in Si III, and Russell's method therefore becomes merely a linear interpolation or extrapolation in this case. It is, nevertheless, worth while to see how far the method is applicable. The relevant data and the results are as follows :—

	Al II.	Si III.	Ratio.		Al II.	Si III.	Ratio.
$2s$ . .	60589	116660	1·926	1S . .	147107	(246200)	(1·674)
$1p_1$.	114281	216904	1·898	1P . .	87262	(170600)	(1·954)
$2p_1$.	46393	94700	2·041	2P . .	43759	(89580)	(2·046)

The interpolated ratios and singlet terms for Si III are shown in brackets. The value for 1S involves a long extrapolation and may be much in error.

It is possible that more exact values, assuming the method of ratios to be valid, may be obtained by plotting the logarithms of the ratios against the logarithms of the terms. This procedure gives 1S = 267000, 2S = 105600, 1P = 169200, 2P = 89740.

The most appropriate line for 1S — 1P in any reasonable accordance with the above calculations is that at λ 1206·9 (ν = 82857) ; this is by far the strongest singlet in the range λ 1400 — λ 990, and may be adopted with considerable confidence.

For the identification of the resonance line 1 S — $1\,p_2$ we have $1\,p_2$ = 217140, and the above calculated values of 1 S give the wave-numbers 29060 and 49860. The limits are wide, but there are no strong singlets near this range except λ 3590 (ν = 27844), λ 3486 (ν = 28670), λ 2559 (ν = 39063), and λ 2541 (ν = 39330). Of these, there can be little hesitation in selecting the last as the most probable resonance line. Its physical behaviour is precisely in accordance with this view, as it is more strongly developed in the ordinary spark than any of the other lines, just as the resonance line of Al II suggested by Russell makes its appearance in the arc, and that of Mg I in the flame.

The identification of the resonance line, and the consequent deduction as to the third ionisation potential, is of considerable importance for astrophysical investigations, and further checks on the line adopted may accordingly be mentioned. If the logarithms of the values of 1S — $1p_2$ be plotted against the logarithms of the $1p_2$ terms for Mg I, Al II and Si III, the value of 1S — $1p_2$ for Si III is given as ν = 41700, which is in sufficient agreement with the adopted line ν = 39330. A similar procedure gives 1S — 1P for Si III = 83000, almost in exact agreement with the adopted line 82857.

Again, if the resonance lines of Na I, Mg II, Al III and Si IV be plotted against the corresponding nuclear charges, or numbers increasing by unity, the points lie very nearly on a straight line. If a similar relation holds for Mg I, Al II, Si III, the value of $1S - 1p_2$ for Si III will be less than 43530, as will appear from the data given below.

	$1\sigma - 1\pi$.	Δν.
Na I	16973	
		18788
Mg II	35761	
		18157
Al III	53918	
		17822
Si IV	71740	

	$1S - 1p_2$.	Δν.
Mg I	21870	
		10830
Al II	32700	
Si III	(< 43530)	

Thus, although it is not to be considered as fully established, there are substantial grounds for the adoption of ν 82857 as the $1S - 1P$ line, and of ν 39330 as the $1S - 1p_2$ line of Si III. If the identification be correct, the terms 1 S and 1 P may then be deduced as follows :—

$$\begin{aligned} 1S - 1p_2 &= 39330 \\ 1p_2 &= 217142 \\ & \ 256472 = 1S \\ 1S - 1P &= 82857 \\ & \ 173615 = 1P \end{aligned}$$

Plausible assignments of other lines of the singlet series might be made, but it is considered desirable to defer the further discussion until more complete silicon data are available for the extreme ultra-violet, and it becomes possible to derive further assistance from the singlet series of Al II.

The above values for $1S - 1p_2$ and 1S suggest that the resonance and ionisation potentials of Si III are respectively 4·85 volts and 31·66 volts, but these values cannot yet be considered final.

There can be no doubt, however, that the spectrum of Si III is generally similar to the spectra of Al II and Mg I, consisting of singlets and triplets, and having 1S for the largest term. As in Al II and Mg I, it may accordingly be concluded that the series electron in Si III normally occupies a 3_1 orbit.

VII. THE SERIES SYSTEM OF Si IV (Si^{+++}).

Details of the observations and analysis of the spectrum of Si IV having already been communicated to the Society,* it is only necessary to summarise the chief results for convenient comparison with the spectra at other stages of ionisation.

The constant for the series was definitely proved to be 16R, in accordance with BOHR's theory, and the whole system was shown to be similar in structure to the doublet series of Al III, Mg II, and Na I, for which the series constants are respectively 9R, 4R, and R. With increase in the value of the series constant, however, the spectrum is displaced as a whole towards shorter wave-lengths. Thus, the brighter component of the first principal pair of lines in Na I is at λ 5889·9, in Mg II at λ 2795·5, in Al III at 1854·7, and in Si IV at λ 1393·9. The chief series of Si IV lie in the extreme ultra-violet, those which appear in the ordinary range of observation being secondary series such as occur in the far infra-red in Na I.

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* *Loc. cit.*

It may also be noted that the separations Δ ν of the first principal pairs are 17·88 for Na I, 91·55 for Mg II, 238 for Al III, and 460 for Si IV.

The various spectral terms of Si IV, with the notation of the present paper, are given in Table IX, calculated terms being enclosed in brackets.

TABLE IX.—The Series Terms of Si IV.

RYDBERG Numbers.	σ.	π_2.	π_1.	δ.	ϕ.	γ.	κ.	BOHR Numbers.
1	364117	292837	292377					3
2				203705				
	170105	145817	145655					4
3				114076	109923			
	98666	87580	87505					5
4				72594	70366	70213		
	[64401]	[58438]	[58397]					6
5				[50186]	48862	48788	48733	
	[45319]	[41766]	[41741]					7
6				[36741]	35893	35835	[35800]	
	[33638]	[31335]	[31319]					8
7				[28050]	[27476]			

The largest term is the 1σ term, from which it follows that the series electron in Si IV normally occupies a 3_1 orbit, as in Al III, Mg II, and Na I. The corresponding ionisation potential of Si IV, representing the energy required to expel the fourth of the outermost electrons from the silicon atom when three of them have already been removed, is 44·95 volts.

The lines of Si IV which have been classified in series are included in Tables X and XIII. The positions of several lines as calculated from the series terms given in Table IX have been included, and it will be seen that nearly all of these have since been confirmed by the observations of BOWEN and MILLIKAN* or of McLENNAN and SHAVER.†

VIII. GENERAL CONCLUSIONS.

(1) The investigation has shown that the changes in the spectrum of silicon which accompany appropriate increases in the energy of the exciting source represent successive

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* ‘Phys. Review,’ vol. 23, p. 1 (1924).

† ‘Trans. Roy. Soc. Canada,’ vol. 18, p. 1 (1924).

ionisations of the silicon atom. This has been established through the identification of four successive systems of spectral series, which are respectively characterised by the series constants R, 4R, 9R and 16R, in accordance with the theory of BOHR.

(2) The spectrum of the neutral atoms (Si I) includes singlets and triplets. The singlets include PS and PD series, which have a common limit about 60072. Only one *ps* and one *pd* triplet have been certainly identified, and the triplet limits are not yet satisfactorily determined. There is no reasonable doubt, however, that the largest term of the spectrum is a *p* or P term, and it is concluded that the series electron normally moves in a 3_2 orbit. The ionisation potential cannot be less than 7·5 volts.

(3) The spectrum of singly-ionised atoms (Si II, or Si^+) includes a doublet system analogous with that of neutral aluminium. Lines at λλ 1533·55, 1526·83 (νν 65208, 65495) form the leading pair of the sharp series, the limits of which are 131531 and 131818. The resonance potential is therefore 8·09 volts and the second ionisation potential 16·27 volts. Besides the usual sets of terms, there is a double term of *d* type, $x_1 = 76498$, $x_2 = 76514$, which yields a strong series of fundamental type in the far ultra-violet; no corresponding terms have been noted in aluminium. The largest term is a π term, and on BOHR's theory it follows that the series electron in Si II normally occupies a 3_2 orbit.

(4) The spectrum of doubly-ionised silicon (Si III or Si^{++}) is of the same type as that of Al II or Mg I, including triplets and singlets. The limits of the triplet series are 216879, 217142, and 217273. The singlet series have not yet been certainly traced, but there is evidence that the resonance line, $1S - 1p_2$, is ν 39330, while the first principal line, $1S - 1P$, is ν 82857. If so, the resonance potential would be 4·85 volts, and the ionisation potential 31·66 volts. As the largest term is 1S it may be concluded that the series electron normally traverses a 3_1 orbit, as in Mg I.

(5) The spectrum of trebly-ionised silicon (Si IV, or Si^{+++}), as shown in a previous paper, forms a doublet system similar to that of Al III, Mg II, and Na I. The leading pair of lines, corresponding with the "D" lines of neutral sodium, is formed by λλ 1393·9, 1402·9. Some of the series of Si IV which appear within the range of observation with ordinary instruments correspond with lines which occur in the far infra-red in neutral sodium. The resonance and ionisation potentials deduced from the observed series are respectively 8·86 and 44·95 volts. The series electron in Si IV normally moves in a 3_1 orbit.

The author desires to express his indebtedness to those who have assisted at various times in the experimental work which forms the basis of the foregoing paper. Many of the earlier photographs with the large quartz spectrograph, including those reproduced in Plate 2, were taken by Mr. J. S. CLARK; Prof. H. DINGLE and Miss E. O'CONNOR have contributed several photographs with the concave grating; and the work with the vacuum spectrograph was mainly carried on by Messrs. H. BARRELL and L. J. FREEMAN.

TABLE X.—General Catalogue of Silicon Lines in the Region λ 6700 — λ 2000.

Wave-lengths, Intensities and Groups.				Wave-Numbers.	Series.
Si I	Si II.	Si III.	Si IV.		
	6671·88 (3)			14984·15	
	6660·49 (2)			15009·77	
	6371·359 (8)			15690·90	II $2\sigma - 2\pi_2$
	6347·091 (10)			15750·90	II $2\sigma - 2\pi_1$
	5978·970 (7)			16720·63	II $2\pi_1 - 3\sigma$
	5957·612 (5)			16780·61	II $2\pi_2 - 3\sigma$
5948·548 (5)				16806·18	
	5915·266 (1)			16900·74	
	5868·404 (3)			17035·70	
	5867·497 (1)			17038·38	
	5846·12 (0)			17100·63	
	5827·80 (0)			17154·38	
	5806·75 (2)			17216·57	
	5800·48 (1)			17235·19	
5797·855 (3)				17242·98	
	5794·58 (0)			17252·73	
5793·070 (3)				17257·23	
	5785·64 (1)			17279·39	
5780·378 (1)				17295·12	
5772·142 (2)				17319·80	
		5739·762 (8)		17417·51	
5708·400 (5)				17513·19	
	5706·375 (1)			17519·41	
	5701·375 (1)			17534·77	
5701·101 (1)				17535·61	
5690·424 (2)				17568·52	
	5688·856 (2)			17573·37	
5684·488 (3)				17586·87	
	5669·590 (4)			17633·07	
5665·554 (1)				17645·64	
	5660·72 (0)			17660·71	
5645·609 (2)				17707·97	
	5639·492 (2)			17727·18	
	5633·00 (0)			17747·61	
	5576·61 (1)			17927·07	
	5540·74 (0)			18043·14	
	5496·24 (1)			18189·21	
	5473·09 (0)			18266·15	
	5468·92 (2)			18280·08	
	5466·93 (0)			18286·73	
	5456·11 (2)			18322·99	
	5454·43 (0)			18328·63	
	5447·10 (0)			18353·31	
	5438·41 (1)			18382·63	
	5432·63 (0)			18402·19	
	5428·73 (0)			18415·41	
	5405·06 (0)			18496·05	
	5294·97 (1)			18880·61	
	5202·51 (3)			19216·15	
	5192·75 (1)			19252·27	
	5185·09 (1)			19280·72	
	5181·77 (1)			19293·07	

TABLE X (continued).

Wave-lengths, Intensities and Groups.				Wave Numbers.	Series.
Si I.	Si II	Si III.	Si IV.		
	5056·353 (2)			19771·60	II $2\pi_1 - 3\delta_2$
	5056·020 (10)			19772·90	II $2\pi_1 - 3\delta_1$
	5041·063 (8)			19831·58	II $2\pi_2 - 3\delta_2$
	4921·69 (1)			20312·57	
	4906·88 (1n)			20373·87	
	4882·98 (0n)			20473·59	
	4859·28 (1)			20573·45	
		4828·923 (4n)		20702·79	III $3f_1 - 4g$
		4819·740 (3n)		20742·23	III $3f_2 - 4g$
		4813·290 (2n)		20770·02	III $3f_3 - 4g$
		4716·658 (5)		21195·99	
		4683·774 (2)		21344·35	
	4683·018 (2)			21347·79	
		4665·87 (0)		21426·25	
	4656·80 (1)			21467·97	
			4654·14 (4n)	21480·25	IV $4\gamma - 5\kappa$
			4631·38 (3n)	21585·80	IV $4\phi - 5\gamma$
		4574·777 (4)		21852·99	III $2s - 2p_3$
		4567·872 (7)		21886·01	III $2s - 2p_2$
		4552·654 (9)		21959·17	III $2s - 2p_1$
			4212·44 (3)	23732·43	IV $4\delta - 5\phi$
	4198·174 (2)			23813·18	
	4190·738 (3)			23855·46	
	4130·884 (10)			24201·08	II $2\delta_1 - 3\phi$
	4128·053 (8)			24217·69	II $2\delta_2 - 3\phi$
			4116·104 (8)	24287·99	IV $2\sigma - 2\pi_2$
4102·945 (5)				24365·89	
			4088·863 (10)	24449·80	IV $2\sigma - 2\pi_1$
	4076·78 (1)			24522·27	
	4075·45 (2)			24530·27	
	4016·22 (0n)			24892·02	
	3998·00 (1n)			25005·46	
	3991·77 (2n)			25044·48	
	3977·46 (0n)			25134·59	
		3924·44 (4)		25474·15	
3905·515 (10)				25597·61	
	3862·592 (6)			25882·04	II $mx_2 - 2\pi_2$
	3856·021 (8)			25926·14	II $mx_1 - 2\pi_1$
	3853·657 (3)			25942·05	II $mx_2 - 2\pi_1$
		3806·56 (5)		26263·00	III $2p_1 - 3d_{321}$
		3796·11 (4)		26335·30	III $2p_2 - 3d_{32}$
		3791·41 (3)		26367·96	III $2p_3 - 3d_3$
			3773·13 (3)	26495·69	IV $3\delta - 3\pi_2$
			3762·41 (4)	26571·18	IV $3\delta - 3\pi_1$
		3590·46 (8)		27843·66	
		3486·93 (6)		28670·36	
		3482·70 (0n)		28705·2	
	3339·84 (3)			29932·98	II $2\pi_1 - 4\sigma$
	3333·16 (2)			29992·96	II $2\pi_2 - 4\sigma$
		3241·67 (6)		30839·43	III $2p_1 - 3s$
		3234·00 (5)		30912·57	III $2p_2 - 3s$

TABLE X (continued).

Wave-lengths, Intensities and Groups.				Wave-Numbers.	Series.
Si I.	Si II.	Si III.	Si IV.		
		3230·55 (3)		30945·58	III $2p_3 - 3s$
		3210·52 (3)		31138·64	
	3210·04 (3)			31143·30	II $2\pi_1 - 4\delta_{21}$
	3203·89 (2)			31203·07	II $2\pi_2 - 4\delta_2$
	3199·54 (1)			31245·48	
		3196·50 (3)		31275·20	
	3195·40 (0)			31285·96	
	3193·10 (1)			31308·50	
	3188·95 (1)			31349·25	
		3186·01 (2)		31378·18	
		3185·16 (3)		31386·55	
			3165·72 (8)	31579·28	IV $2\pi_1 - 3\delta$
			3161·63 (1)	31620·13	
			3149·56 (6)	31741·30	IV $2\pi_2 - 3\delta$
		3096·786 (4)		32282·21	III $2d_3 - 2p_3$
		3093·613 (3)		32315·31	III $2d_3 - 2p_2$
		3093·423 (6)		32317·31	III $2d_2 - 2p_2$
		3086·620 (1)		32388·51	III $2d_3 - 2p_1$
		3086·429 (3)		32390·53	III $2d_2 - 2p_1$
		3086·225 (7)		32392·67	III $2d_1 - 2p_1$
		3040·93 (1)		32875·14	III $3f_1 - 5g$
		3037·26 (1)		32914·87	III $3f_2 - 5g$
		3034·74 (1)		32942·20	III $3f_3 - 5g$
3020·01 (0)				33102·85	
2987·650 (5)				33461·39	
2970·35 (2)				33656·27	
	2905·70 (3)			34405·06	II $2\delta_1 - 4\phi$
	2904·29 (2)			34421·75	II $2\delta_2 - 4\phi$
			2895·13 (1)	34530·67	IV $4\phi - 6\gamma$
			2887·90 (1)	34617·11	
2881·585 (10R)				34692·97	I 1P − 1S
	2726·74 (2)			36662·99	II $2\pi_1 - 5\sigma$
			2723·81 (1)	36702·30	IV $4\delta - 6\phi$
	2722·29 (1)			36722·91	II $2\pi_2 - 5\sigma$
	2682·27 (2)			37270·80	II $2\pi_1 - 5\delta_{21}$
	2677·98 (1)			37330·50	II $2\pi_2 - 5\delta_2$
			2675·26 (3)	37368·45	
		2659·84 (1)		37585·09	
		2655·87 (2)		37641·26	
			2655·58 (2)	37645·37	
		2640·80 (4)		37856·05	
2631·296 (5)				37992·77	
	2606·09 (1)			38360·21	II $2\sigma - 3\pi_2$
	2604·44 (2)			38384·52	II $2\sigma - 3\pi_1$
2568·66 (2)				38919·15	
		2559·22 (7)		39062·70	
		2546·10 (3)		39263·98	
		2541·83 (10)		39329·92	
2532·39 (2)				39476·52	
2528·516 (10R)				39537·01	I $1p_1 - 1p_2'$
2524·118 (9R)				39605·89	I $1p_2 - 1p_3'$
2519·210 (8R)				39683·03	I $1p_2 - 1p_2'$

Table X (continued).

Wave-lengths, Intensities and Groups.				Wave-Numbers.	Series.
Si I.	Si II.	Si III.	Si IV.		
			2517·56 (5)	39709·04	IV $\rbrace\ 3\phi - 4\gamma$
			2517·48 (5)	39710·30	IV
2516·123 (15R)				39731·73	I $1p_1 - 1p_1'$
2514·331 (7R)				39760·04	I $1p_3 - 1p_2'$
2506·904 (10R)				39877·83	I $1p_2 - 1p_1'$
	2505·07 (0)			39907·01	
	2504·32 (1)			39918·97	
	2501·99 (1)			39956·15	II $2\delta_1 - 5\phi$
	2500·96 (1)			39972·60	II $2\delta_2 - 5\phi$
2452·136 (3)				40768·42	I $1p_1 - 2s$
		2449·53 (2*n*)		40811·79	
2443·378 (3)				40914·54	I $1p_2 - 2s$
2438·782 (3)				40991·64	I $1p_3 - 2s$
2435·159 (8R)				41052·61	I 1P — 1D
		2374·29 (1)		42104·97	
			2371·04 (1)	42162·69	
		2367·00 (1)		42234·65	
		2357·94 (2)		42396·91	
		2357·15 (2)		42411·12	
		2356·25 (3)		42426·77	
		2353·07 (1)		42484·65	
		2350·16 (1)		42537·26	
		2308·18		43310·83	
2303·06 (2)				43407·11	
			2300·90 (0)	43447·85	
			2287·08 (10*d*)	43710·37	IV $3\delta - 4\phi$
2218·917 (1)				45052·96	I $1p_1 - 2d_3$
2218·080 (2)				45069·96	I $1p_1 - 2d_2$
2216·685 (4)				45098·32	I $1p_1 - 2d_1$
2211·750 (2)				45198·92	I $1p_2 - 2d_3$
2210·912 (3)				45216·07	I $1p_2 - 2d_2$
2207·980 (2)				45276·09	I $1p_3 - 2d_3$
	2136·41 (1)			46792·69	
			2127·48 (4)	46989·05	IV $2\pi_1 - 3\sigma$
2124·140 (6R)				47062·94	I 1P — 2S
2123·070 (1)				47086·65	
			2120·19 (3)	47150·62	IV. $2\pi_2 - 3\sigma$
2084·48 (1)				47958·25	
2082·31 (0)				48008·23	
	2072·61 (10)			48232·89	II $mx_1 - 3\phi$
	2071·94 (8)			48248·49	II $mx_2 - 3\phi$
2065·57 (0)				48397·26	
2061·25 (1)				48498·67	
	2058·917 (0)			48553·61	II $2\sigma - 4\pi_2$
	2058·532 (1)			48562·70	II $2\sigma - 4\pi_1$
2058·20 (5R)				48570·51	I 1P — 2D
2054·85 (1)				48649·70	

TABLE XI.—Silicon Lines of Uncertain Groups in the Region λ 6700 — λ 2000.

Si III ?		Si IV ?	
λ, Intensity.	ν.	λ, Intensity.	ν.
4638·12 (1)	21554·44	3622·44 (0)	27597·86
4338·52 (1)	23042·88	3612·26 (1)	27675·63
4183·48 (0)	23896·83	3601·52 (2)	27758·16
3147·38 (0)	31763·28	3525·90 (2)	28353·48
3126·25 (0)	31977·97	3279·25 (0)	30486·02
3077·56 (00)	32483·87	3276·25 (1)	30513·93
3053·18 (1)	32743·25	3258·67 (1)	30678·55
3045·10 (0)	32830·13	3254·79 (00)	30715·11
3043·97 (0)	32842·31	3253·44 (00)	30727·85
3030·00 (0)	32993·73	3216·26 (1)	31083·06
2360·58 (1)	42349·50	3214·65 (0)	31098·63
2360·21 (1)	42356·14	2831·51 (1)	35306·48
2334·60 (1)	42820·73	2817·09 (1)	35487·19
2334·40 (1)	42824·40	2816·15 (1)	35499·04
		2365·05 (0)	42269·47
		2364·34 (0)	42282·16
		2349·51 (1)	42549·03

TABLE XII.—Arc Lines of Silicon (Si I) in the Region λ 2000 — λ 1840.

λ, Intensity.	ν.	Series.	λ, Intensity.	ν.	Series.
1991·80 (1)	50205·8		1901·00 (5R)	52603·9	I 1P — 3S
1988·97 (4)	50277·3	I $1p_1 - 1p_1''$	1892·80 (3R)	52831·8	I 1P — 3D
1986·33 (2)	50344·1	I $1p_1 - 1p_2''$	1881·60 (2)	53146·3	
1983·20 (3)	50423·6	I $1p_2 - 1p_1''$	1880·71 (1)	53171·4	I $1p_1 - 3s$?
1980·56 (2)	50490·8	I $1p_2 - 1p_2''$	1875·54 (2)	53318·0	I $1p_2 - 3s$?
1979·15 (2)	50526·7	I $1p_2 - 1p_3''$	1874·68 (3)	53343·9	
1977·54 (3)	50567·9	I $1p_3 - 1p_2''$	1872·87 (2)	53394·0	I $1p_3 - 3s$?
1962·80 (0)	50947·6		1852·50 (2)	53981·1	
1961·80 (1)	50973·6		1850·84 (1*d*?)	54029·5	
1961·00 (0)	50994·4		1850·07 (00)	54052·0	
1959·92 (1)	51022·5		1848·68 (0)	54092·7	
1958·40 (0)	51062·1		1847·95 (00)	54114·0	
1957·60 (1)	51083·0		1846·05 (00)	54169·7	
1954·71 (2)	51158·5		1845·57 (1n)	54183·8	
1946·64 (1)	51370·6		1843·70 (0)	54238·8	Ca ?
1940·33 (0)	51537·6		1841·25 (1n)	54310·9	
1904·30 (2)	52512·7				

TABLE XIII.—Classified Lines of Si II, Si III, and Si IV in the Region more Refrangible than λ 2000.

λ vac. and Groups.			Wave-numbers.	Series.	Other observations.	
Si II.	Si III.	Si IV.			B. & M.*	McL. & S.†
1817·06 (10)			55034	II $1\pi_1 - x_{12}$		1817·1 (10)
1808·14 (8)			55305	II $1\pi_2 - x_2$		1808·1 (10)
		1797·5 (0)	55633	IV $3\delta - 4\pi_2$		
		1796·1 (1)	55676	IV $3\delta - 4\pi_1$		
		1727·4 (4)	57888	IV $2\pi_2 - 2\delta$		1727·5 (3)
		1722·7 (5)	58050	IV $2\pi_1 - 2\delta$		1722·7 (4)
1711·0 (6*d*?)			58445	II $x_{12} - 4\phi$		
1563·1 (3*d* ?)			63975	II $x_{12} - 5\phi$		
		1533·55	65208	IV $3\delta - 5\phi$		
1533·55 (10)			65208	II $1\pi_1 - 2\sigma$	1533·4 (0)	1533·5 (5)
1526·38 (8)			65495	II $1\pi_2 - 2\sigma$	1526·9 (0)	1526·8 (4)
	1502·00 (5)		66578	III $2d_{123} - 3f_3$		1502·0 (5)
	1501·32 (5)		66608	III $2d_{12} - 3f_2$		1501·3 (5)
	1500·39 (5)		66649	III $2d_1 - 3f_1$		1500·3 (5)
1485·4 (3)			67322	II $x_{12} - 6\phi$		
1438·9 (1)			69498	II $x_{12} - 7\phi$		
1408·8 (0)			70982	II $x_{12} - 8\phi$		
		1402·9 (8)	71280	IV $1\sigma - 1\pi_2$	1403·0 (6)	1402·7 (10)
		1393·9 (10)	71740	IV $1\sigma - 1\pi_1$	1393·9 (6)	1393·6 (10)
		[1368·72]‡	[73061]	IV $2\pi_1 - 4\delta$		1369·1 (1)
		[1365·69]	[73223]	IV $2\pi_2 - 4\delta$		1365·0 (2)
	1303·57 (2)		76712	III $1p_2 - p'_2$	1303·5 (1)	1303·3 (6)
	1301·32 (2)		76845	III $1p_2 - p'_3$		1301·2 (6)
	1299·10 (4)		76976	III $\left\{\begin{matrix} 1p_2 - p'_2 \\ 1p_1 - p'_1 \end{matrix}\right.$	1299·0 (2)	1298·9 (7)
	1296·86 (2)		77109	III $1p_3 - p'_2$		
	1294·69 (2)		77239	III $1p_2 - p'_1$	1294·9 (1)	1294·5 (6)
		[1279·05]	78183	IV $3\delta - 6\phi$		
1265·04 (10)			79040	II $1\pi_1 - 2\delta_{12}$	1264·9 (1)	1264·7 (6)
1260·66 (8)			79324	II $1\pi_2 - 2\delta_2$	1260·5 (1)	1260·4 (5)
		[1230·71]	[81254]	IV $2\pi_1 - 4\sigma$		
		[1228·26]	[81416]	IV $2\pi_2 - 4\sigma$	1228·1 (0)	1227·7 (3)
		[1211·75]	[82525]	IV $2\sigma - 3\pi_2$		
		[1210·65]	[82600]	IV $2\sigma - 3\pi_1$		1210·5 (3)
	1206·9 (10)		82857	III 1S − 1P	1206·5 (5)	1206·6 (10)
1197·79 (3)			83487	II $1\pi_1 - 2\pi'_2$		
1194·89 (5)			83690	II $1\pi_1 - 2\pi'_1$	1194·4 (0)	
1193·62 (3)			83779	II $1\pi_2 - 2\pi'_2$		
1190·80 (4)			83977	II $1\pi_2 - 2\pi'_1$		
		[1154·73]	[86600]	IV $3\delta - 7\phi$		1154·5 (0)
	1144·85 (1)		87348	III $2d_1 - 4f_1$?		1144·8 (2)
	1142·74 (0)		87509	III $2d_{12} - 4f_2$?		
		[1127·75]	[88672]	IV $1\pi_1 - 2\delta$	1128·4 (2)	1128·1 (8)
		[1121·93]	[89132]	IV $1\pi_2 - 2\delta$	1122·6 (2)	1122·2 (8)
	1113·76 (5)		89786	III $1p_1 - 2d$	1113·5 (2)	1113·0 (8)
	1110·47 (5)		90052	III $1p_2 - 2d$	1110·3 (2)	1109·7 (7)
	1108·85 (4)		90184	III $1p_3 - 2d$.	1108·9 (2)	1108·2 (6)

* BOWEN and MILLIKAN, *loc. cit.* † McLENNAN and SHAVER, *loc. cit.*

‡ Figures in brackets represent calculated lines.

TABLE XIII (continued).

λ vac. and Groups.			Wave-numbers.	Series.	Other observations.	
Si II.	Si III.	Si IV.			B. & M.	McL. & S.
		1066·3 (8)*	93782	IV $2\delta - 3\phi$	1066·7 (0)	1066·4 (8)
[1023·75]			[97680]	II $1\pi_1 - 3\sigma$		
[1020·75]			[97967]	II $1\pi_2 - 3\sigma$		
	997·70 (1)		100230	III $1p_1 - 2s$	997·5 (0)	997·4 (4)
	995·23 (0)		100479	III $1p_2 - 2s$	994·6 (0)	994·7 (4)
	[993·94]		[100610]	III $1p_3 - 2s$		
993·09 (1)			100696	II $1\pi_1 - 3\delta_{12}$		
990·32 (0)			100977	II $1\pi_2 - 3\delta_2$		
		[859·52]	[111667]	IV $2\sigma - 4\pi_2$		
		[859·25]	[111708]	IV $2\sigma - 4\pi_1$		
		[817·85]	[122272]	IV $1\pi_1 - 2\sigma$	818·0 (2)	818·0 (7)
		[814·78]	[122732]	IV $1\pi_2 - 2\sigma$	815·0 (2)	814·8 (7)
		[779·19]	[128339]	IV $2\sigma - 5\pi_2$		778·7 (0)
		[779·03]	[128364]	IV $2\sigma - 5\pi_1$		
		[749·97]	[133339]	IV $2\delta - 4\phi$		749·7 (3)
		[645·82]	[154843]	IV $2\delta - 5\phi$		646·0 (1)
		[560·85]	[178301]	IV $1\pi_1 - 3\delta$		561·1 (1)
		[559·41]	[178761]	IV $1\pi_2 - 3\delta$		
		[458·09]	[218300]	IV $1\sigma - 2\pi_2$	457·7 (3)	457·8 (0)
		[457·75]	[218462]	IV $1\sigma - 2\pi_1$		
		[361·615]	[276537]	IV $1\sigma - 3\pi_2$	361·6 (1)	
		[361·517]	[276612]	IV $1\sigma - 3\pi_1$		

* This line does not occur in the vacuum arc; it was originally adopted from Millikan's observations of the vacuum spark of carbon.

Description of Plates.

The photographs which are reproduced are mainly intended to illustrate progressive changes in the spectrum of silicon, as observed in vacuum tubes of silicon tetrafluoride with discharges of varying intensity. In each set of spectra the effect of a comparatively feeble discharge is shown at the bottom and of the strongest discharge at the top.

Lines which are known to be due to fluorine, or are probably to be attributed to that element, are marked beneath the uppermost spectrum. Typical lines belonging to the four spectra of silicon are also indicated.

The photographs in Plates 1 and 2, and the first three on Plate 3, were taken with a large quartz spectrograph, Hilger's E 1.

Plate 1.—Region λ 7000 to λ 3400. The predominant lines in this región belong to Si I, Si II, and Si III.

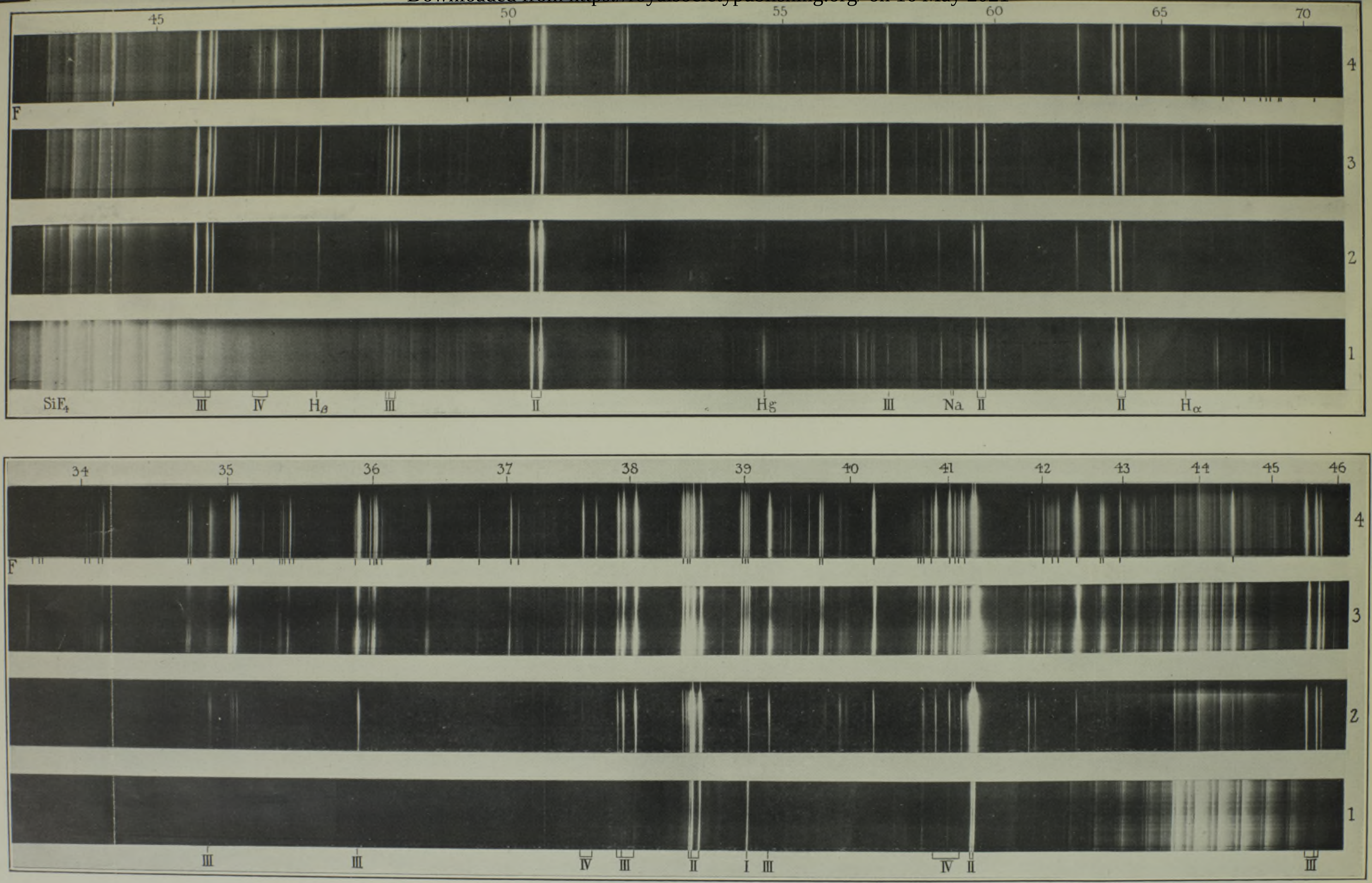
Plate 2.—Region λ 4000 to λ 2800.—The capillary tube was rather wider than that used for the spectra in Plate 1, and the lines are more sharply defined. A few faint lines of argon which appeared in No. 1 have been obliterated in the reproduction.

Plate 3.—(1), (2), (3): Vacuum tube spectra of SiF_4 in the region λ 2800 to λ 2400.

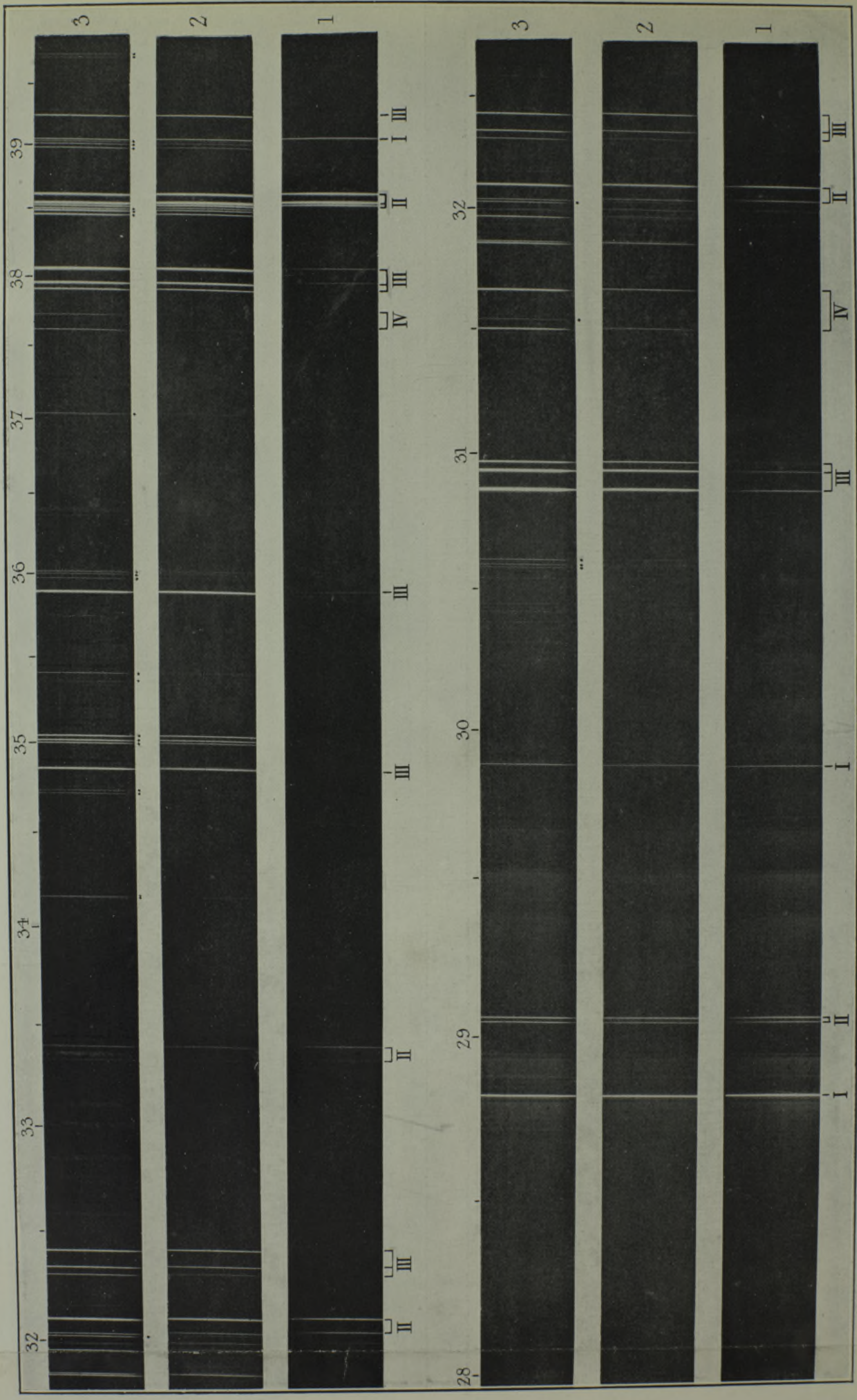
(4): Arc spectrum of fused silicon in the region λ 2300 to λ 1840, with aluminium spark comparison. Taken with a small quartz spectrograph by BELLINGHAM and STANLEY.

(5), (6): Spark spectrum of fused silicon in an atmosphere of hydrogen, region λ 1900 to λ 1250. A small amount of self-induction was introduced for No. 5, and it will be noted that the principal pair of Si IV, λλ 1393, 1402, is considerably reduced in intensity. Lines of aluminium and other impurities are present in these spectra.

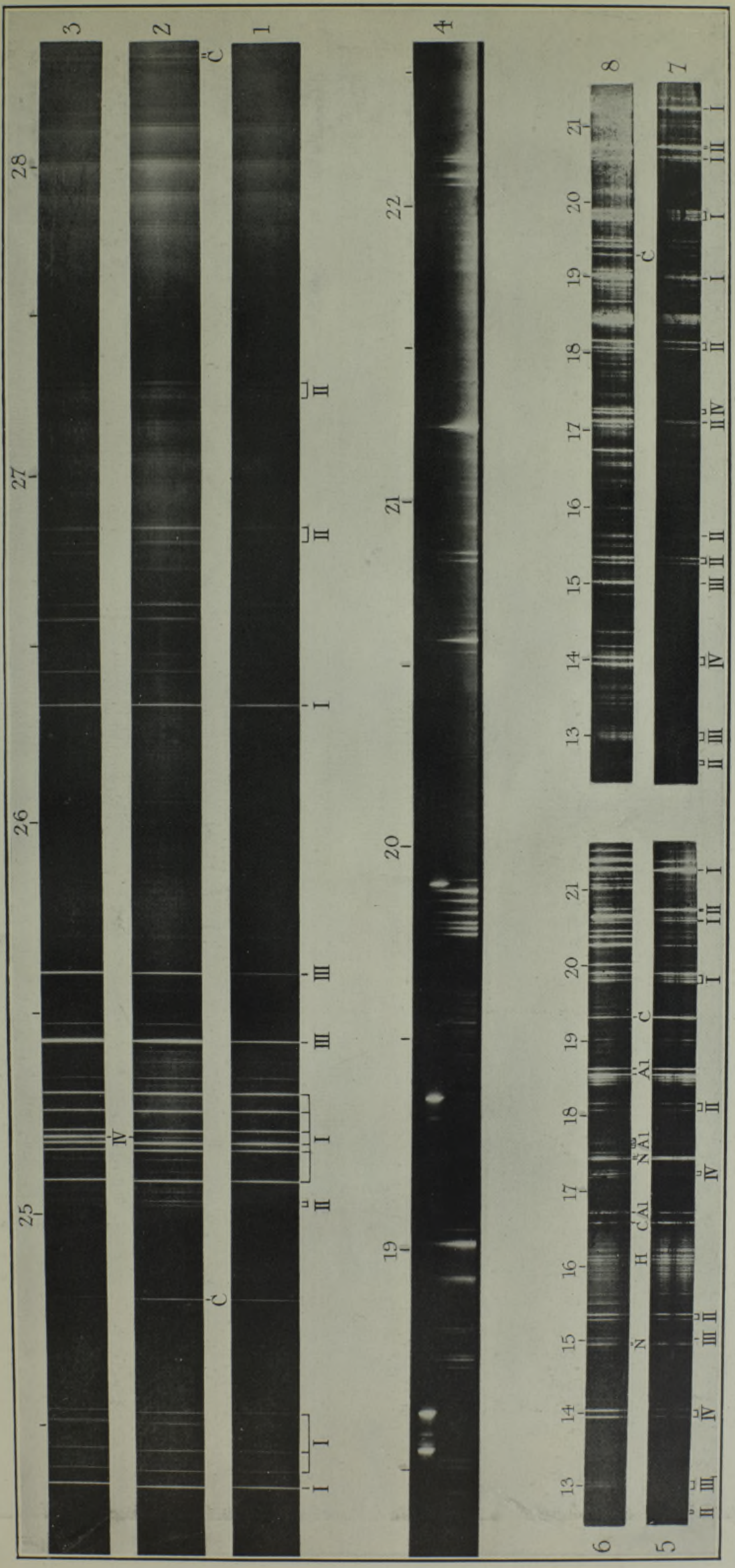
(7), (8): Vacuum tube spectra of SiF_4 in the region λ 1900 to λ 1250. The discharge was strongest for No. 8, in which lines of Si III and Si IV are most strongly developed.



Progressive Spectra of Silicon (Si F_4 Vacuum tube).



Progressive Spectra of Silicon (Si F$_4$ Vacuum tube).



Spectra of Silicon: 3, 2, 1, 7, 8, Si F_4 Vacuum tube. 4, Arc. 5, 6, Spark in Hydrogen.